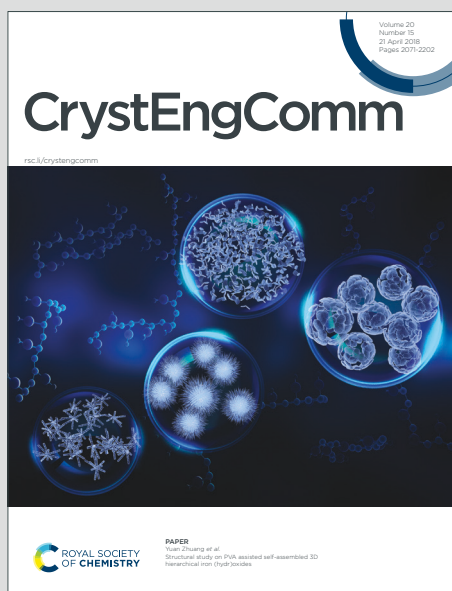


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# Supramolecular architectures sustained by delocalised C–I $\cdots\pi$ (arene) interactions in molecular crystals and the propensity of their formation<sup>†</sup>

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## ABSTRACT

A systematic analysis of the Cambridge Crystallographic Database has been made for supramolecular architectures sustained by C–I $\cdots\pi$ (chelate ring) interactions where the iodide atom is directed towards the ring centroid, C<sub>g</sub>, of the arene ring, *i.e.* with the angle subtended at the iodide atom, C–I $\cdots$ C<sub>g</sub> ( $\theta$ ) being  $\geq 160^\circ$ . The majority of the 181 identified aggregates are one-dimensional chains of varying topology (100 examples) followed by zero-dimensional aggregates (71 examples) with only a small number of two-dimensional arrays (4 examples). The overall likelihood for the formation of these delocalised interactions is around 4%, a number that increases to around 15% when the angle  $\theta$  restriction is relaxed to  $90^\circ$ . A comparison has been made with the formation of C–X $\cdots\pi$ (chelate ring) interactions for the lower (X =) bromide, chloride and fluoride congeners. This shows these interactions are more likely to form in the order X = I > Br > Cl >> F.

<sup>†</sup> Electronic supplementary information (ESI) available. See DOI:10.1039/xxxx

## Introduction

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It is well-established that arene rings can play pivotal roles in the supramolecular organisation of molecular compounds in the condensed-phase<sup>1,2</sup> and have long attracted interest owing to their impact in chemistry and biology endeavours.<sup>3,4</sup> The magnitude of parallel stacking interactions between arene rings can be moderated by substitution patterns,<sup>5,6</sup> the degree of offset<sup>7,8</sup> and whether the arene ring is involved in coordination to a metal centre.<sup>9,10</sup> Naturally, other entities can interact with arene rings with the most notable being hydrogen, giving rise the archetypal T-shaped or end-on C–H $\cdots\pi$ (arene) interactions.<sup>11–13</sup> Arene rings can also interact with alkyl residues,<sup>14</sup> metal centres, be they neutral,<sup>15,16</sup> cationic<sup>17–20</sup> or anionic,<sup>21–23</sup> lone-pairs of electrons<sup>24–26</sup> and of the latter, prominent examples among these species are halides.

The  $\sigma$ -hole (polar cap) model<sup>27–32</sup> has emerged as a unifying concept to provide an explanation for some of the aforementioned contacts which, at first sight, suggest attractive interactions between like-charged species, *e.g.* lone-pair $\cdots\pi$ (arene) and halide $\cdots\pi$ (arene) interactions. In its simplest description and relevant to the work described herein, *i.e.* an evaluation of C–I $\cdots\pi$ (arene) interactions in crystals, a  $\sigma$ -hole can be described as a region of reduced electronic density for the halide (X) atom at the extension of a C–X bond. If the electronic density is low, as in the case of an iodide atom, positive electrostatic potential will be associated with this site, and it is this which can form an attractive interaction with an electron-rich system, such as an arene ring. Far from being a crystallographic curiosity restricted to molecular structures, C–X $\cdots\pi$ (arene), for X = F, Cl, Br and I, interactions play real roles in chemistry and biology.

The interactions between halides with biological molecules is well-documented<sup>33–36</sup> and have important ramifications for drug discovery and the delineation of mechanisms of action.<sup>37–</sup>

<sup>39</sup> The important biological roles notwithstanding, intramolecular C–I $\cdots\pi$ (arene) interactions

occurring at the stereogenic centre are proposed as being crucial in the stabilisation of a key intermediate in the reaction mechanism leading to the formation of difluorinated  $\beta$ -substituted styrenes,<sup>40</sup> C–I $\cdots\pi$ (arene) interactions are vital in the uptake of molecular iodine in metal-organic frameworks<sup>41</sup> and covalent organic frameworks,<sup>42</sup> and in moderating band structure formation in semi-conducting complexes of SnCl<sub>4</sub>.<sup>43</sup> In a very recent application, C70-decorated chromatography columns were able to alter the retention times of variously substituted halobenzene molecules and the strength of the C–X $\cdots\pi$ (arene) interactions enabling this behaviour shown to be in the order F < Cl < Br < I.<sup>44</sup>

The aforementioned  $\sigma$ -hole model of bonding along the extension of the C–X bond for C–X $\cdots\pi$ (arene) interactions does not preclude other modes of approach of X to an arene ring. Thus, complementing the end-on approach, where the C–X $\cdots$ ring-centroid(arene) angle approaches 180°, is a side-on approach where, at the other extreme, the C–X $\cdots$ ring-centroid(arene) angle approaches 90°, and implies a X(lone-pair) $\cdots\pi$ (arene) interaction.<sup>45,46</sup> Indeed, a classification for the different geometries associated with interaction of an entity with an arene ring exists in the literature,<sup>47,48</sup> namely, delocalised, for an end-on approach, semi-localised in circumstances where the approaching entity is directed to a specific  $\pi$ -bond of the ring, and localised where the entity is directed to one atom of the ring only. While a localised contact might be indicative of a  $\pi$ -hole interaction,<sup>31,49</sup> there is not necessarily a direct relationship between a geometry of approach and the mode of bonding as seen recently in a Br $\cdots\pi$ (arene) contact which was described as a simultaneous  $\sigma$ -hole/ $\pi$ -hole interaction.<sup>50</sup>

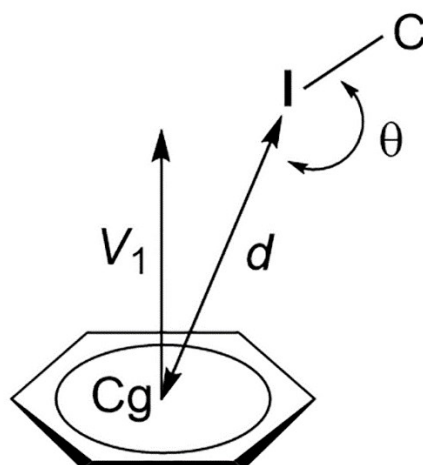
Before proceeding further, it is appropriate to make some comments on the energy of stabilisation provided by delocalised C–I $\cdots\pi$ (arene) interactions in crystals where they are formed. Given the interest in this type of interaction, classified among the general class of halogen bonding interactions,<sup>51</sup> it is not surprising there are a number of thorough studies directed towards this question, both experimentally and through computational chemistry

investigations.<sup>52-56</sup> For example, the calculated energy of stabilisation for a delocalised C–I $\cdots\pi$ (arene) interaction for a pair of C<sub>6</sub>H<sub>5</sub>I molecules in the gas-phase is 3.63 kcal/mol.<sup>57</sup> The cited studies show energies in the range from 1.29 to 3.63 kcal/mol and it is acknowledged the strongest of these interactions can be competitive with other halogen bonding interactions and indeed hydrogen bonding.<sup>54,58,59</sup> The nature of the C–X $\cdots\pi$ (arene) interaction is mainly dispersive with smaller contributions from coulombic attraction and charge-transfer, and these terms are at a maximum for the least electronegative iodide atom, which accounts for the relative strength of C–X $\cdots\pi$ (arene) interactions, *i.e.* X = I > Br > Cl >> F.

With the foregoing in mind and in connection of on-going studies of the interactions of arene rings involving non-traditional donors/acceptors, *e.g.* element(lone-pair) $\cdots\pi$ (arene),<sup>60</sup> C–H $\cdots\pi$ (chelate-ring)<sup>61,62</sup> and C–Cl $\cdots\pi$ (chelate-ring),<sup>63</sup> herein, a survey of the formation of delocalised C–I $\cdots\pi$ (arene) interactions is made along with a description of the supramolecular architectures they sustain and an assessment of the propensity of such interactions to form in molecular crystals of iodide-containing analogues and in comparison in the crystals of their bromide, chloride and fluoride congeners.

## Methods

The CSD<sup>64</sup> (version 5.41, two updates) was searched for C–I $\cdots\pi$ (chelate) contacts employing *ConQuest* (version 2.0.4)<sup>65</sup> employing the protocols indicated in Fig. 1. The vector normal to the plane through the arene ring with the origin at the ring centroid, C<sub>g</sub>, is  $V_1$ . The value of  $\theta$  is the angle subtended at the iodide atom by the carbon atom to which it is attached and C<sub>g</sub>. The value of  $\theta$  was constrained to lie between 160 and 180° to determine the presence of a delocalised C–I $\cdots\pi$ (arene) contact.<sup>47,48</sup> The other constraint was,  $d$ , the distance between C<sub>g</sub> and the iodide atom. The value of  $d$  was set to 3.88 Å, being the sum of the van der Waals radius of iodide, *i.e.* 1.98 Å,<sup>66</sup> and that assumed for an arene ring, *i.e.* 1.90 Å.<sup>67</sup>



**Fig. 1** An illustration of the search protocols employed for the identification of delocalised C–I $\cdots\pi$ (arene) contacts in molecular crystals. The vector,  $V_1$ , is the normal to the plane through the arene ring with the origin at the ring-centroid (Cg),  $d$  is the separation between Cg and the iodide atom, and  $\theta$  is the angle subtended at the iodide atom by the carbon atom it is bound to and Cg.

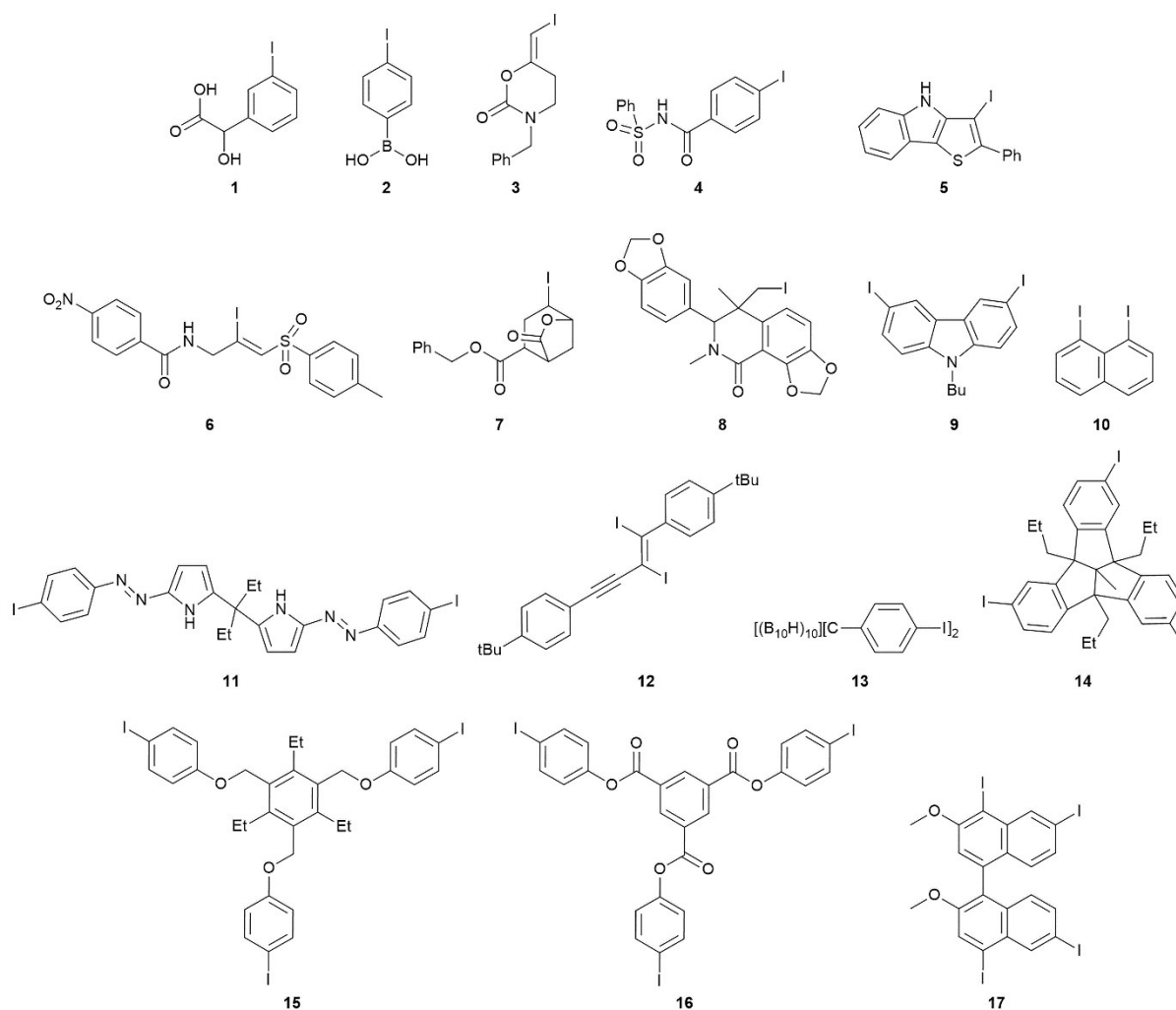
Additional constraints were applied to the search in that structures with  $R > 0.075$ , were polymeric or suffered from errors and/or disorder were excluded as were heavy element-containing structures. All 233 retrieved hits were evaluated manually to ensure the identified C–I $\cdots\pi$ (arene) contact was operating independently of other non-covalent interactions, most notably hydrogen bonding; duplicates were also removed. The data analysis was performed employing both PLATON<sup>68</sup> and DIAMOND,<sup>69</sup> with all diagrams generated with the latter. After sorting, there were 181 crystals featuring supramolecular architectures sustained primarily by C–I $\cdots\pi$ (arene) interactions. As the purpose of the present survey is directed towards an analysis of the role of C–I $\cdots\pi$ (arene) interactions upon supramolecular aggregation patterns, full descriptions of the three-dimensional packing are not given. The exception to this is in usually only in circumstances where C–I $\cdots\pi$ (arene) interactions outside the search criteria are apparent. The structures are divided into single-molecule containing crystals and

multi-component crystals. Within each category, zero-dimensional aggregation patterns are discussed before one- and two-dimensional examples. Within each classification, molecules with one iodide atom are described before those with two iodide atoms, *etc.* Similarly, aggregates sustained by a single C–I $\cdots$  $\pi$ (arene) interaction between molecules are discussed before those featuring two or more interactions per molecule. Within each category of structures, aggregates are ordered in terms of increasing values of  $d$ . Images of all aggregation patterns, values of  $d$  and  $\theta$  for each contact along with full details of crystal composition are given in ESI Tables 1-8.

## Supramolecular architectures

### Zero-dimensional aggregates sustained by a single C–I $\cdots$ $\pi$ (arene) interaction

There are 17 structures in this category and the chemical diagrams for the interacting species are given in Fig. 2. The common feature of each of **1**,<sup>70</sup> **2**,<sup>71</sup> **3**,<sup>72</sup> **4**,<sup>73</sup> **5**,<sup>74</sup> **6**,<sup>75</sup> **7**<sup>76</sup> and **8**<sup>77</sup> is the presence of a single iodide atom in the molecule and at least two independent molecules in the crystallographic asymmetric unit. In this structural motif, a single C–I $\cdots$  $\pi$ (arene) interaction is formed between two independent molecules leading to a zero-dimensional aggregate; in **1**, there are three independent molecules and two of these are connected by a single C–I $\cdots$  $\pi$ (arene) contact. A representative aggregate for this motif is illustrated in Fig. 3(a) for **5**.<sup>74</sup> Several of the aggregates, exemplified by **4**<sup>73</sup> in Fig. 3(b), are orientated to allow for a second, putative C–I $\cdots$  $\pi$ (arene) interaction leading to a dimeric aggregate sustained by two such interactions. However, the geometric parameters characterising the second contact are outside of the specified search criteria for this survey. In the case of **4**, while the value of  $d = 3.6406(16)$  Å is within the distance limit, the  $\theta$  angle of  $146.42(12)^\circ$  is outside the specified angle range; similar angular deviations are noted in the crystals of **3**<sup>72</sup> and **6**<sup>75</sup> – the geometric parameters for these interactions are included in ESI Table 1.

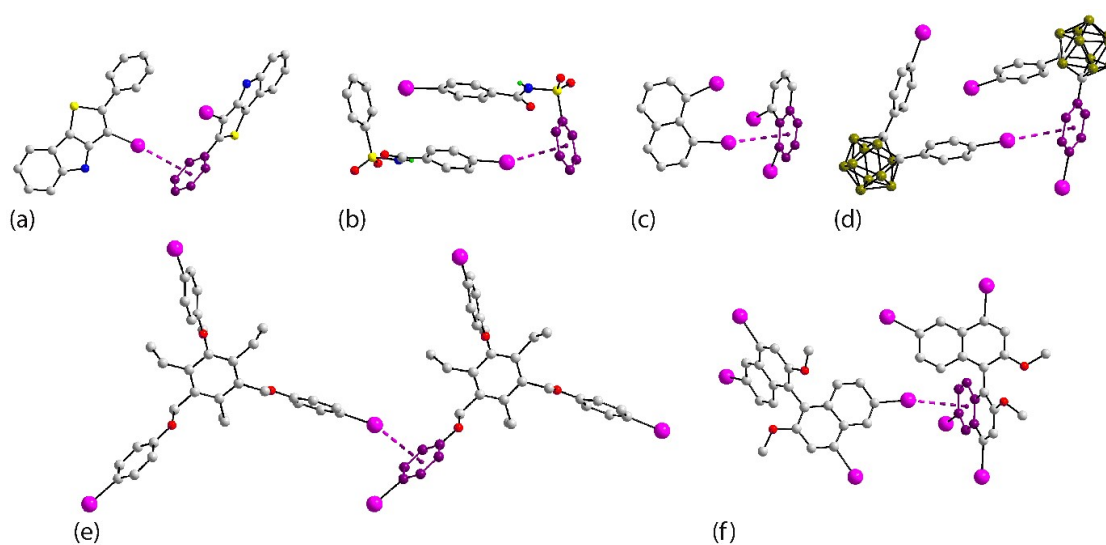


**Fig. 2** Chemical diagrams for molecules **1-17** which form zero-dimensional aggregates in their crystals sustained by a single delocalised C-I $\cdots\pi$ (arene) interaction. Compound **13** is bis(4-iodophenyl)-o-carborane.

Five molecules, *i.e.* **9**,<sup>78</sup> **10**,<sup>79</sup> **11**,<sup>80</sup> **12**<sup>81</sup> and **13**,<sup>82</sup> feature two iodide atoms in their molecular formula. In each two-molecule aggregate formed in the respective crystal, sustained by a C–I $\cdots\pi$ (arene) interaction, only one of the iodide atoms participates in the contact. In **9**, four independent molecules comprise the asymmetric unit but, only two of these are connected to form a two-molecule aggregate *via* a C–I $\cdots\pi$ (arene) interaction. In **10**, Fig. 3(c), there are six independent molecules but, again, only two of these associate *via* a C–I $\cdots\pi$ (arene)



interaction. In **11–13**, the  $\text{C-I}\cdots\pi(\text{arene})$  connection is made between the two independent molecules comprising the asymmetric unit. In **13**,<sup>82</sup> Fig. 3(d), the alignment of the molecules suggests a second contact but, the parameters defining this are outside the search criteria, ESI Table 1. There are three molecules having three iodide atoms and as for other aggregates in this section, all associate *via* a single  $\text{C-I}\cdots\pi(\text{arene})$  interaction. In **14**,<sup>83</sup> there are four independent molecules and two of these associate to form a dimeric aggregate. The other two molecules associate in a similar fashion but with  $d$  beyond the sum of the van der Waals radii, ESI Table 1. In **15**,<sup>84</sup> Fig. 3(e), the dimeric aggregates thus formed are assembled into a twisted chain when contacts beyond the search criteria are taken into consideration. In the crystal of **16**,<sup>85</sup> additional  $\text{C-I}\cdots\pi(\text{arene})$  interactions outside the search criteria complemented by  $\text{I}\cdots\text{O}=\text{C}$  halogen bonding interactions lead to a hexagonal array, as described in the original report.<sup>85</sup> In the last structure to be discussed in this section, only one of the four iodide atoms in the tetra-iodide molecule, **17**,<sup>86</sup> forms a  $\text{C-I}\cdots\pi(\text{arene})$  interaction, occurring between the two independent molecules comprising the asymmetric unit, Fig. 3(f).



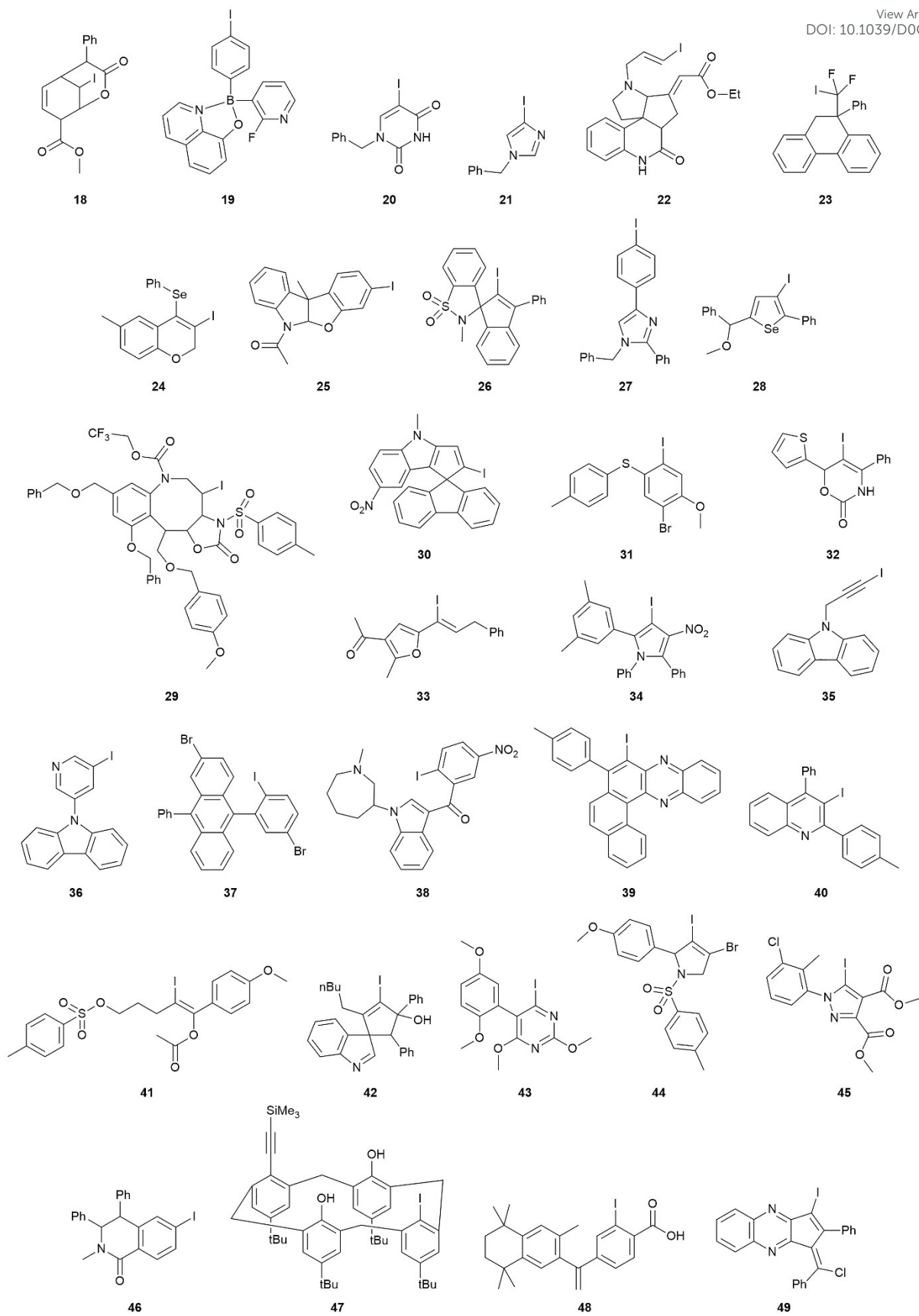
**Fig. 3** Supramolecular aggregation in zero-dimensional aggregates sustained by a single C–I⋯ $\pi$ (arene) interaction, represented as a pink-purple dashed line, in: (a) **5**, (b) **4**, (c) **10**, (d) **13**, (e) **15** and (f) **17**. Colour code for this and subsequent molecular structures diagrams: iodide, pink; sulphur, yellow; oxygen, red; nitrogen, blue; carbon, grey; olive-green, boron; hydrogen, green. The arene ring participating in the C–I⋯ $\pi$ (arene) contact is shown in purple. Non-acidic hydrogen atoms are omitted for clarity.

### Zero-dimensional aggregates sustained by two C–I⋯ $\pi$ (arene) interactions

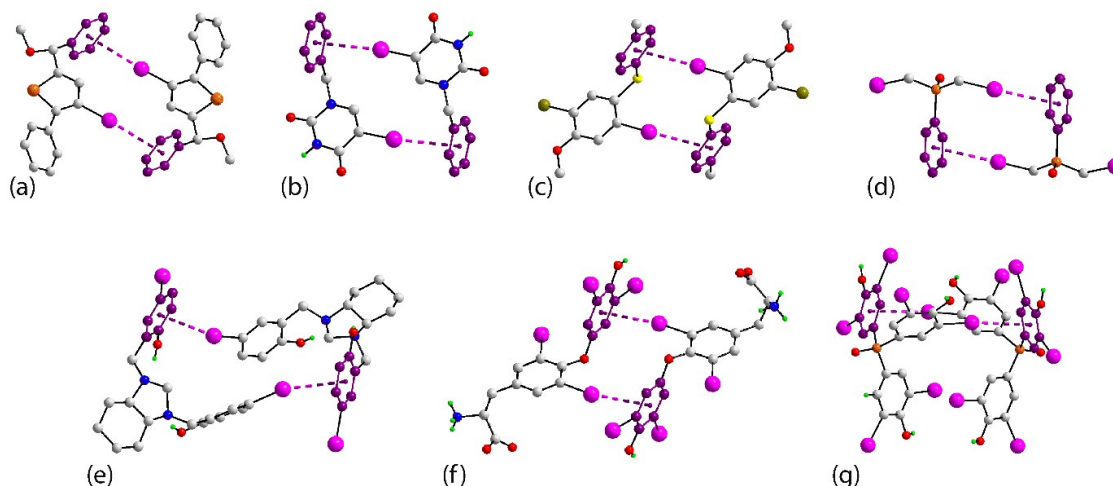
There are 32 molecules forming very similar dimeric aggregates in their crystals, Fig. 4, each sustained by a pair of C–I⋯ $\pi$ (arene) interactions. These are, in order of increasing values of  $d$ , **18**,<sup>87</sup> **19**,<sup>88</sup> **20**,<sup>89</sup> **21**,<sup>90</sup> **22**,<sup>91</sup> **23**,<sup>92</sup> **24**,<sup>93</sup> **25**,<sup>94</sup> **26**,<sup>95</sup> **27**,<sup>96</sup> **28**,<sup>97</sup> **29**,<sup>98</sup> **30**,<sup>99</sup> **31**,<sup>100</sup> **32**,<sup>101</sup> **33**,<sup>102</sup> **34**,<sup>103</sup> **35**,<sup>104</sup> **36**,<sup>105</sup> **37**,<sup>106</sup> **38**,<sup>107</sup> **39**,<sup>108</sup> **40**,<sup>109</sup> **41**,<sup>110</sup> **42**,<sup>111</sup> **43**,<sup>112</sup> **44**,<sup>113</sup> **45**,<sup>114</sup> **46**,<sup>115</sup> **47**,<sup>116</sup> **48**<sup>117</sup> and **49**,<sup>118</sup> details are collated in ESI Table 2. All of aforementioned dimeric aggregates are disposed about a centre of inversion with a representative example, *i.e.* **28**,<sup>97</sup> shown in Fig. 5(a). In **20**,<sup>89</sup> two independent molecules comprise the asymmetric unit, and each of these assembles about a centre of inversion with one dimeric aggregate shown in Fig. 5(b). A comment on the values of  $d$  and  $\theta$  in **20**<sup>89</sup> is apt. For the illustrated molecule in Fig. 5(b),  $d = 3.566(4)$  Å and  $\theta = 166.2(3)^\circ$ , and these compare with  $d = 3.791(5)$  Å and  $\theta = 173.8(3)^\circ$  for the second dimeric aggregate, indicating the shorter value of  $d$  is not correlated with a more linear approach of the C–H vector to the ring centroid, Cg. Two independent molecules also comprise the asymmetric unit of in each of **23**<sup>92</sup> and of **36**.<sup>105</sup> In each of these crystals, only one of the independent molecules self-associates about a centre of inversion to form a dimeric aggregate; the second independent molecule is similarly orientated but, with parameters outside the search criteria, see ESI Table 2. Despite having the common feature of two independent molecules in the crystallographic asymmetric unit, a different situation pertains in the crystals of each of

**30**<sup>99</sup> and **42**.<sup>111</sup> In these crystals, while one of the independent molecules in each crystal forms a dimer across a centre of inversion, the second independent molecule does not form analogous C–I $\cdots\pi$ (arene) interactions at all, even outside the search criteria. The dimeric aggregate in the crystal of **31**,<sup>100</sup> Fig. 5(c), is notable in that there is also a bromide substituent in the molecule. Similarly, molecules in **37**<sup>106</sup> and **44**<sup>113</sup> feature bromide substituents. The presence of both iodide and bromide atoms in these crystals suggest a possible competition between the formation of C–I $\cdots\pi$ (arene) and C–Br $\cdots\pi$ (arene) interactions. In neither **31** nor **44** is there evidence of C–Br $\cdots\pi$ (arene) interactions. However, **37**, where there are two bromide substituents in the molecule, a C–Br $\cdots\pi$ (arene) interaction, with  $d = 3.4843(19)$  Å and  $\theta = 151.16(17)^\circ$ , is apparent and complements the C–I $\cdots\pi$ (arene) contact. In each of **45**<sup>114</sup> and **49**<sup>118</sup> with chloride substituents, C–Cl $\cdots\pi$ (arene) interactions are not observed in their crystals.

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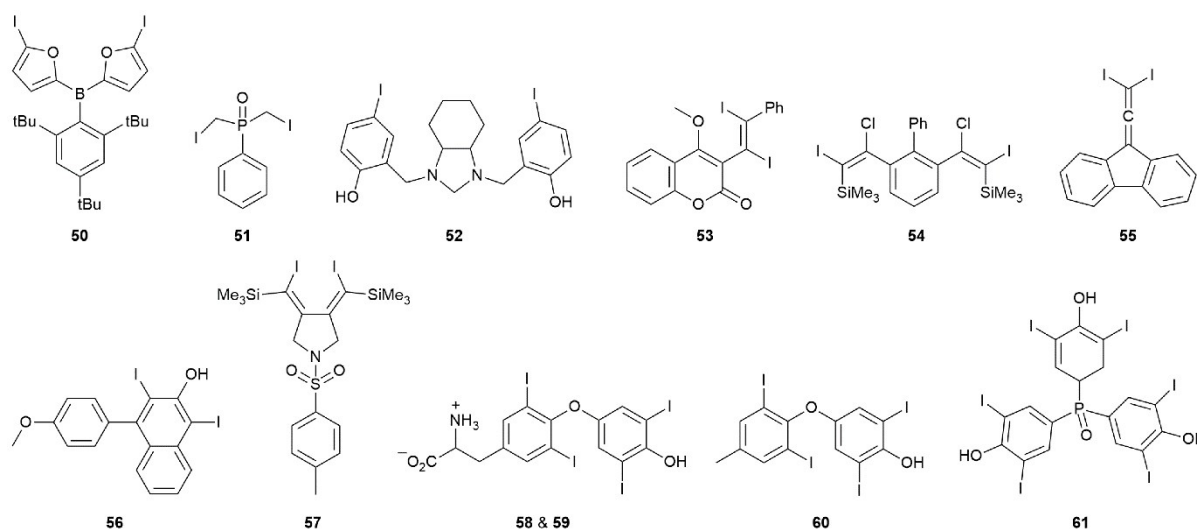
**Fig. 4** Chemical diagrams for molecules **18-49** which form zero-dimensional aggregates in their crystals sustained by two C–I $\cdots\pi$ (arene) interactions.



**Fig. 5** Supramolecular aggregation in zero-dimensional aggregates sustained by a two C–I $\cdots\pi$ (arene) interactions: (a) **28**, (b) **20**, (c) **31**, (d) **51**, (e) **52**, (f) **58** and (g) **61**. Extra colour code: selenium, orange; bromide, dark-green.

The molecules in **50**,<sup>119</sup> **51**,<sup>120</sup> **52**,<sup>121</sup> **53**,<sup>122</sup> **54**,<sup>123</sup> **55**,<sup>124</sup> **56**<sup>125</sup> and **57**<sup>126</sup> each carry two iodide substituents, see Fig. 6 for chemical diagrams. A greater variety of supramolecular association is apparent in this series, at least in terms of the symmetry associated with the resulting aggregates. When a dimeric aggregate is formed, it is always sustained by a pair of C–I $\cdots\pi$ (arene) interactions. Three of the crystals feature a single molecule in the asymmetric unit, and each of these self-associates about a centre of inversion to form a dimeric aggregate, namely in the crystals of **51**,<sup>120</sup> Fig. 5(d), **54**<sup>123</sup> and **56**.<sup>125</sup> Again with a single molecule in the asymmetric unit, the aggregates in **52**,<sup>121</sup> Fig. 5(e), and **57**<sup>126</sup> are disposed about a 2-fold axis of symmetry. In each of **53**<sup>122</sup> and **55**,<sup>124</sup> two molecules comprise the asymmetric unit. One of these in each crystal forms a centrosymmetric dimer *via* C–I $\cdots\pi$ (arene) interactions whereas the second independent molecule does not form C–I $\cdots\pi$ (arene) interactions. A different

situation pertains in the crystal of **50**<sup>119</sup> where three independent molecules comprise the asymmetric unit. One of these forms a centrosymmetric dimer whereas the other two associate *via* a pair of C–I $\cdots\pi$ (arene) interactions. One of the C–I $\cdots\pi$ (arene) interactions within the non-symmetric dimer has  $d = 3.4948(14)$  Å and  $\theta = 164.56(11)^\circ$ . A longer separation, *i.e.*  $d = 3.6428(15)$  Å is noted in the centrosymmetric dimer but, the angle is closer to linearity, *i.e.*  $\theta = 172.29(11)^\circ$ .



**Fig. 6** Chemical diagrams for molecules **50-61** which form zero-dimensional aggregates in their crystals sustained by two C–I $\cdots\pi$ (arene) interactions.

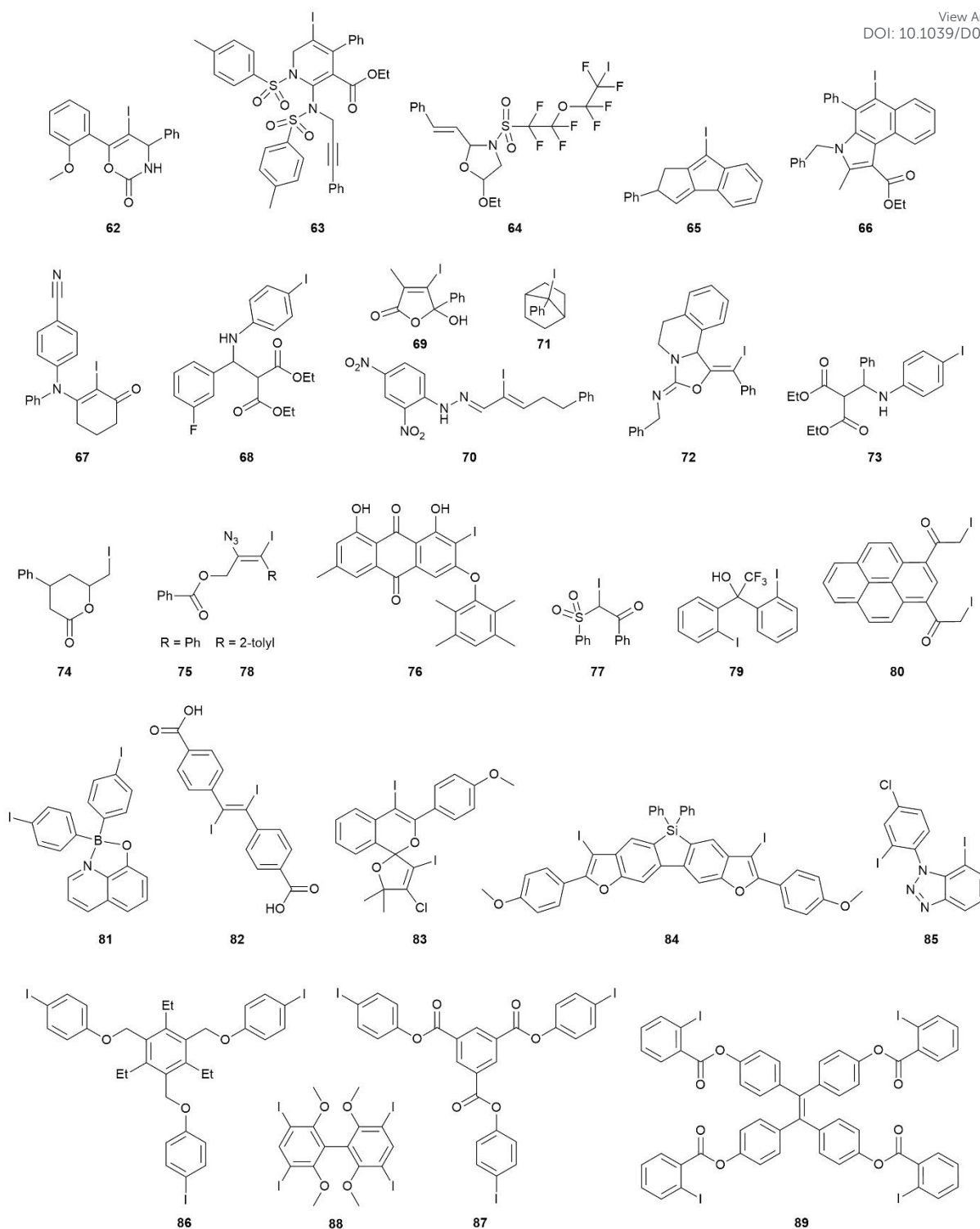
In zwitterions **58**, Fig. 5(f), and **59**,<sup>127</sup> which differ in the number of co-crystallised water molecules in their crystals, and in **60**,<sup>128</sup> Fig. 6, there are four iodide atoms available for forming C–I $\cdots\pi$ (arene) interactions yet, only one does so in each case. The asymmetric unit in the crystals of each of **58** and **59**<sup>127</sup> comprises two independent molecules and in each case, these associate *via* a pair of non-equivalent C–I $\cdots\pi$ (arene) interactions; in **60**,<sup>128</sup> the dimer is centrosymmetric. Despite there being six iodide atoms in the molecular formula of **61**,<sup>129</sup> Fig. 6, only one C–I $\cdots\pi$ (arene) interaction falls within the search criteria. This leads to the two-molecule aggregate disposed about a 2-fold axis of symmetry illustrated in Fig. 5(g).

## Linear, one-dimensional supramolecular chains sustained by C–I $\cdots$ $\pi$ (arene)

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### interactions

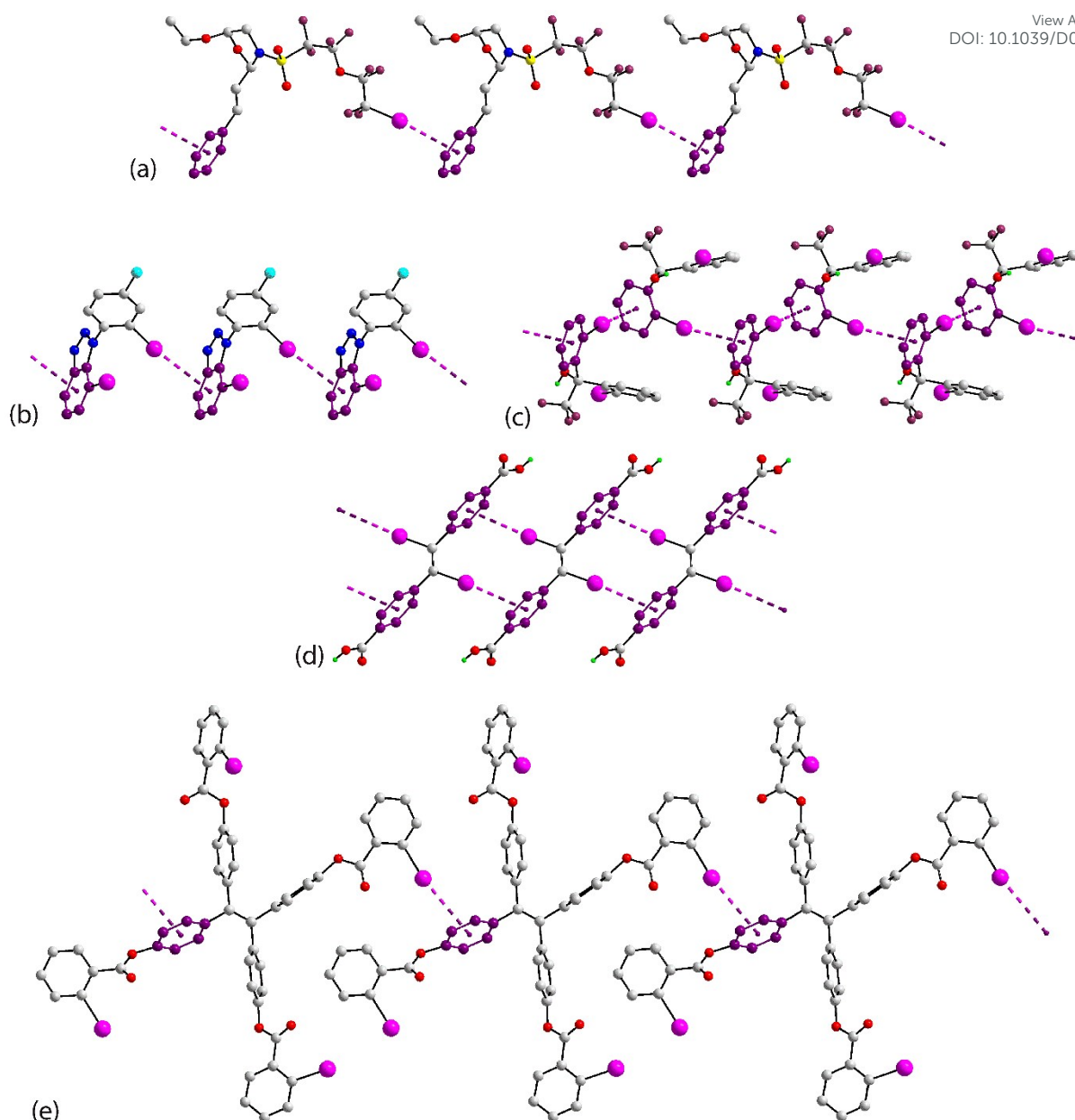
There are 17 molecules forming a linear, one-dimensional supramolecular chains sustained by an average of one C–I $\cdots$  $\pi$ (arene) interaction per repeat unit in their crystals: **62**,<sup>101</sup> **63**,<sup>130</sup> **64**,<sup>131</sup> **65**,<sup>132</sup> **66**,<sup>133</sup> **67**,<sup>134</sup> **68**,<sup>135</sup> **69**,<sup>136</sup> **70**,<sup>137</sup> **71**,<sup>138</sup> **72**,<sup>139</sup> **73**,<sup>135</sup> **74**,<sup>140</sup> **75**,<sup>141</sup> **76**,<sup>142</sup> **77**<sup>143</sup> and **78**,<sup>141</sup> see Fig. 7 for their chemical diagrams. A representative chain is shown in Fig. 8(a), namely for heteroatom-rich **64**.<sup>131</sup> With one exception, all crystals but that of **66**<sup>133</sup> have one molecule in the asymmetric unit. In the exceptional example, **66**,<sup>133</sup> there are two independent molecules. Each of these self-assembles into a linear chain but, for one of the independent molecules, the geometric parameters characterising the C–I $\cdots$  $\pi$ (arene) interaction are outside of the search limits for delocalised C–I $\cdots$  $\pi$ (arene) interactions. The structure of **77**<sup>143</sup> is notable in that, being published in 1986, is the earliest structure described in this survey featuring an intermolecular, delocalised C–I $\cdots$  $\pi$ (arene) interaction in its crystal.



**Fig. 7** Chemical diagrams for molecules **62-89** which form linear, one-dimensional chains in their crystals sustained by a single C-I... $\pi$ (arene) interaction per repeat unit.



Linear, one-dimensional supramolecular chains sustained by an average of one C–I $\cdots\pi$ (arene) interaction per repeat unit are also evident in the crystals of molecules **79**,<sup>144</sup> **80**,<sup>145</sup> **81**,<sup>146</sup> **82**,<sup>147</sup> **83**<sup>148</sup> and **84**,<sup>149</sup> each having two iodide substituents; see Fig. 7 for chemical diagrams. The linear supramolecular chain in **84**<sup>149</sup> is illustrated in Fig. 8(b) and in common with **80**,<sup>145</sup> **82**<sup>147</sup> and **83**<sup>148</sup> has one molecule per asymmetric unit. In **79**,<sup>144</sup> Fig. 8(c), two independent molecules comprise the asymmetric unit and these assemble into a two-molecule aggregate *via* a single C–I $\cdots\pi$ (arene) interaction with  $d = 3.516(4)$  Å and  $\theta = 161.0(2)^\circ$ . The dimeric aggregates thus formed, assemble into a linear chain *via* a second C–I $\cdots\pi$ (arene) interaction. The values of  $d = 3.620(4)$  Å and  $\theta = 174.0(2)^\circ$  associated with the latter interaction again show there is no direct correlation between  $d$  and the linearity of the approach of the iodide atom to the ring-centroid. Two molecules comprise the asymmetric unit of **81**<sup>146</sup> but, only one of these assembles into a linear chain. A variation occurs in the crystal of **85**,<sup>150</sup> Fig. 7, in that, on average, there are two C–I $\cdots\pi$ (arene) interactions per molecule as illustrated in Fig. 8(d). The molecule itself is disposed about a centre of inversion and associates with translationally-related molecules to form the linear chain.



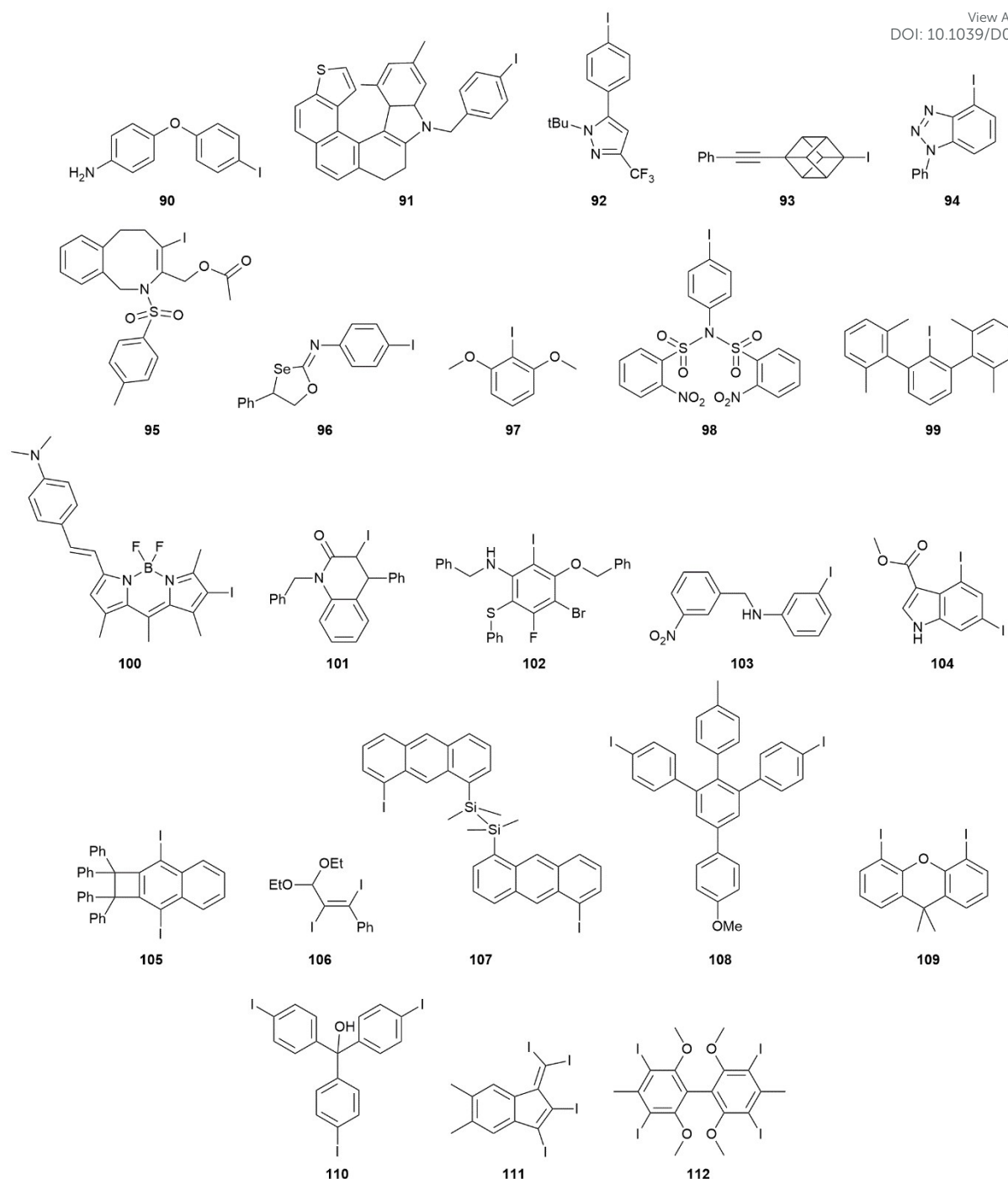
**Fig. 8** Supramolecular aggregation in linear, one-dimensional chains by C–I $\cdots$  $\pi$ (arene) interactions: (a) **64**, (b) **84**, (c) **79**, (d) **85** and (e) **89**. Extra colour code: fluoride, plum.

The next two molecules have three iodide substituents, *i.e.* **86**<sup>151</sup> and **87**,<sup>85</sup> Fig. 7, and each assembles into a linear chain *via* a single C–I $\cdots$  $\pi$ (arene) interaction in a fashion similar to tetra-substituted **88**,<sup>152</sup> and **89**,<sup>153</sup> Fig. 7, with chain for the latter shown in Fig. 8(e). It is noted the non-solvated form of **87**, *i.e.* **16**,<sup>85</sup> associates into a two-molecule aggregate *via* a single C–I $\cdots$  $\pi$ (arene) interaction. There are two independent molecules in the crystal of **89**.<sup>153</sup> The

second independent molecule assemblies as shown in Fig. 8(e) but having  $d = 3.976(4)$  Å and  $\theta = 134.9(2)^\circ$ , with both parameters outside the search criteria. The aggregation in the crystal of **86**,<sup>151</sup> can be compared with that in the solvent-free form, *i.e.* **15**,<sup>84</sup> Fig. 3(e), in which a two-molecule aggregate assembled *via* a single C–I $\cdots\pi$ (arene) interaction is observed. Each of the remaining iodide atoms in **87**,<sup>85</sup> also participates in a C–I $\cdots\pi$ (arene) interaction but, with geometric parameters outside the search criteria, see ESI Table 3. If these interactions are considered, a flat, two-dimensional array is realised.<sup>76</sup>

### **Zig-zag, one-dimensional supramolecular chains sustained by C–I $\cdots\pi$ (arene) interactions**

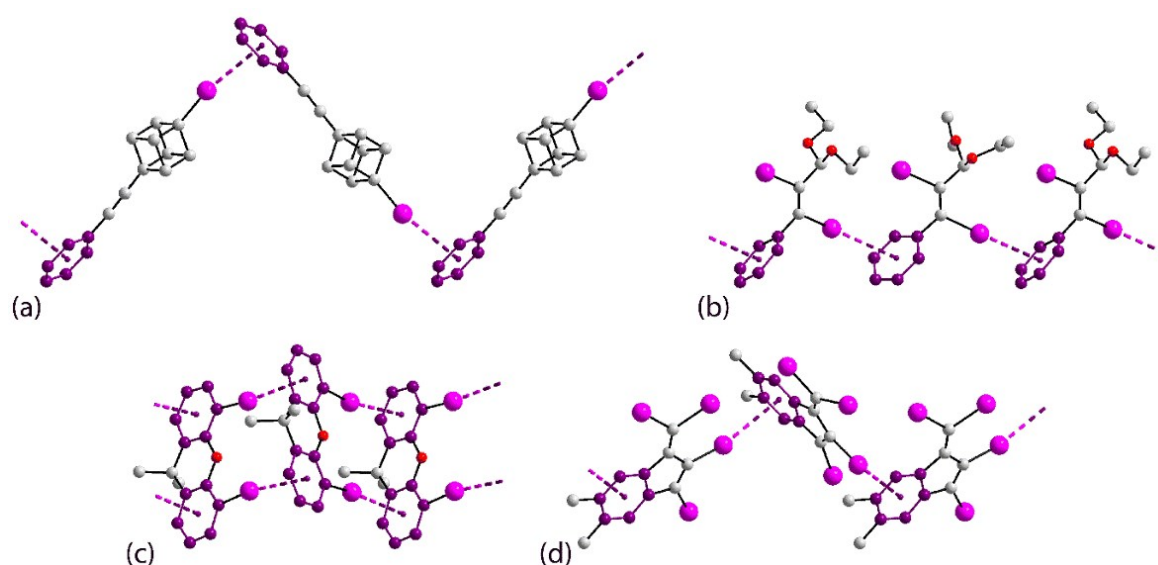
In this section, there are 14 examples of molecules bearing a single iodide atom forming an average of one C–I $\cdots\pi$ (arene) interaction per molecule to form a one-dimensional chain with a zig-zag topology. The chemical structures for these molecules, *i.e.* **90**,<sup>154</sup> **91**,<sup>155</sup> **92**,<sup>156</sup> **93**,<sup>157</sup> **94**,<sup>149</sup> **95**,<sup>158</sup> **96**,<sup>159</sup> **97**,<sup>160</sup> **98**,<sup>161</sup> **99**,<sup>162</sup> **100**,<sup>163</sup> **101**,<sup>164</sup> **102**,<sup>165</sup> and **103**,<sup>166</sup> are shown in Fig. 9. The common feature of all supramolecular zig-zag chains is their propagation by crystallographic glide symmetry, see ESI Table 4. A representative chain in the crystal of **93**<sup>157</sup> is shown in Fig. 10(a). With two exceptions, the asymmetric unit comprises one independent molecule. The deviations from this generalisation are found in **92**<sup>156</sup> and **97**<sup>160</sup> where half the molecule comprises the asymmetric unit in each case owing to crystallographically-imposed mirror symmetry in the molecule. The crystal of **99**<sup>162</sup> is of interest in that this is one of two examples of polymorphic structures in this review. While **99**<sup>162</sup> is orthorhombic (*Pbca*), a monoclinic form (*C2/c*) is also known,<sup>167</sup> in which there are no notable C–I $\cdots\pi$ (arene) interactions.



**Fig. 9** Chemical diagrams for molecules **90-112** which form zig-zag, one-dimensional chains in their crystals sustained by a C–I $\cdots\pi$ (arene) interactions.

The next six molecules, *i.e.* **104**,<sup>168</sup> **105**,<sup>169</sup> **106**,<sup>170</sup> **107**,<sup>171</sup> **108**<sup>172</sup> and **109**,<sup>173</sup> each have two iodide atoms in their molecular formula, Fig. 9. The first five molecules, exemplified by **106**<sup>170</sup> in Fig. 10(b), feature zig-zag chains propagated by zig-zag symmetry and are sustained

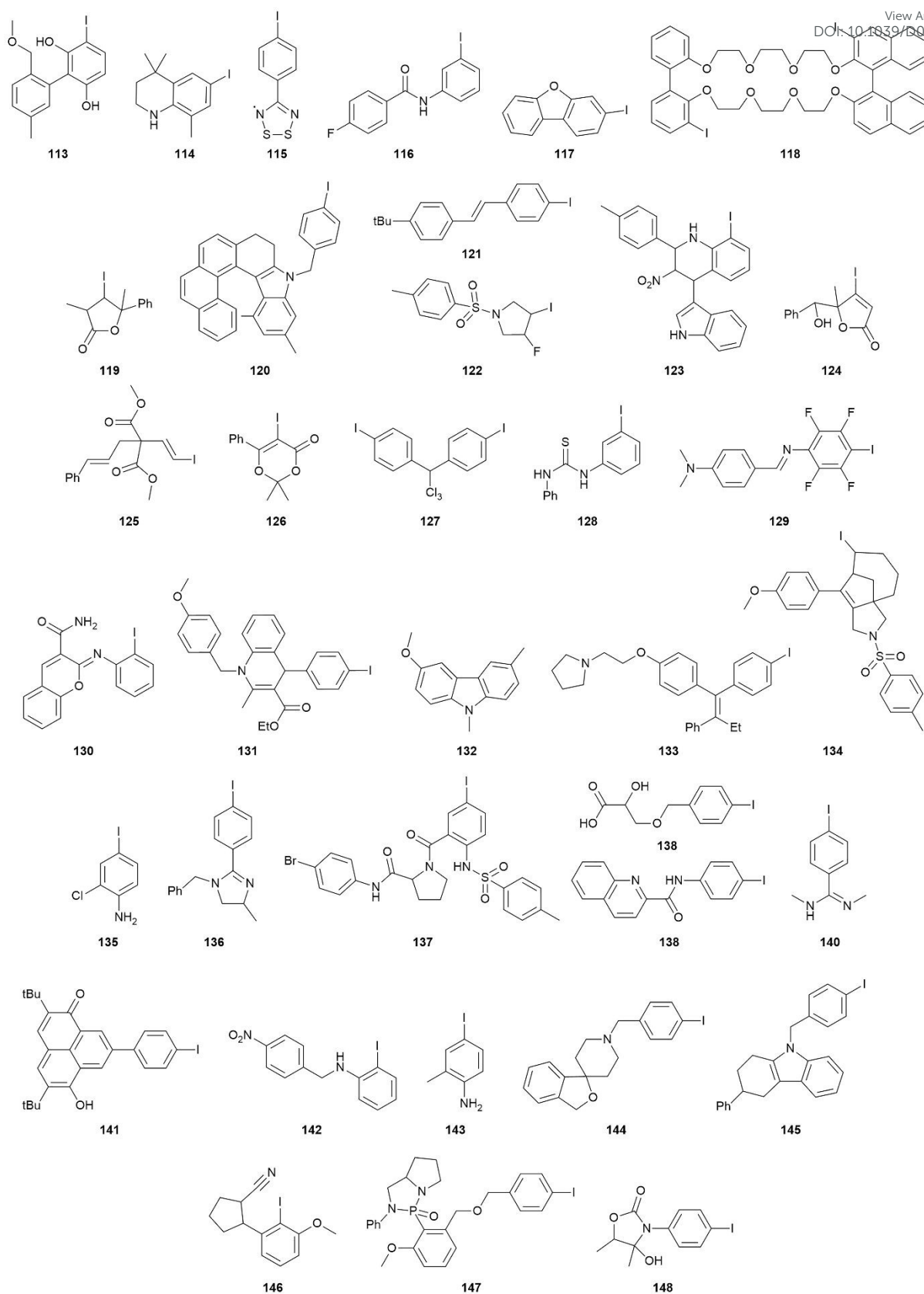
by a single C–I $\cdots\pi$ (arene) interaction, on average, per molecule. A difference occurs in **109**<sup>173</sup> as i), the molecule has mirror symmetry and ii) there are on average two C–I $\cdots\pi$ (arene) interactions per molecule, Fig. 10(c); there is only one other example with as many C–I $\cdots\pi$ (arene) interactions between repeat units among one-dimensional chains, namely, in **85**,<sup>150</sup> illustrated previously in Fig. 8(d). As shown in Fig. 9, the molecule in **110**,<sup>48</sup> contains three iodide atoms and those of **111**<sup>174</sup> and **112**,<sup>175</sup> four. The molecule in **110**<sup>48</sup> has mirror symmetry and forms a single C–I $\cdots\pi$ (arene) interaction, on average, per molecule with the interacting iodide atom lying on the plane. The zig-zag chain is propagated by glide-symmetry. The arene rings related across the plane also form C–I $\cdots\pi$ (arene) interactions but these are operating in concert with bifurcated O–H $\cdots\pi$  contacts are so are ignored in this survey. In each of **111**,<sup>174</sup> Fig. 10(d), and **112**<sup>175</sup> only one of the four available iodide atoms participates in a delocalised C–I $\cdots\pi$ (arene) interaction to generate a zig-zag chain (glide-symmetry); additional C–I $\cdots\pi$ (arene) interactions are noted in the crystal of **112**<sup>175</sup> but, with geometric characteristics outside the search criteria, see ESI Table 4.



**Fig. 10** Supramolecular aggregation in zig-zag, one-dimensional chains sustained by C–I $\cdots\pi$ (arene) interactions: (a) **93**, (b) **106**, (c) **109** and (d) **111**.

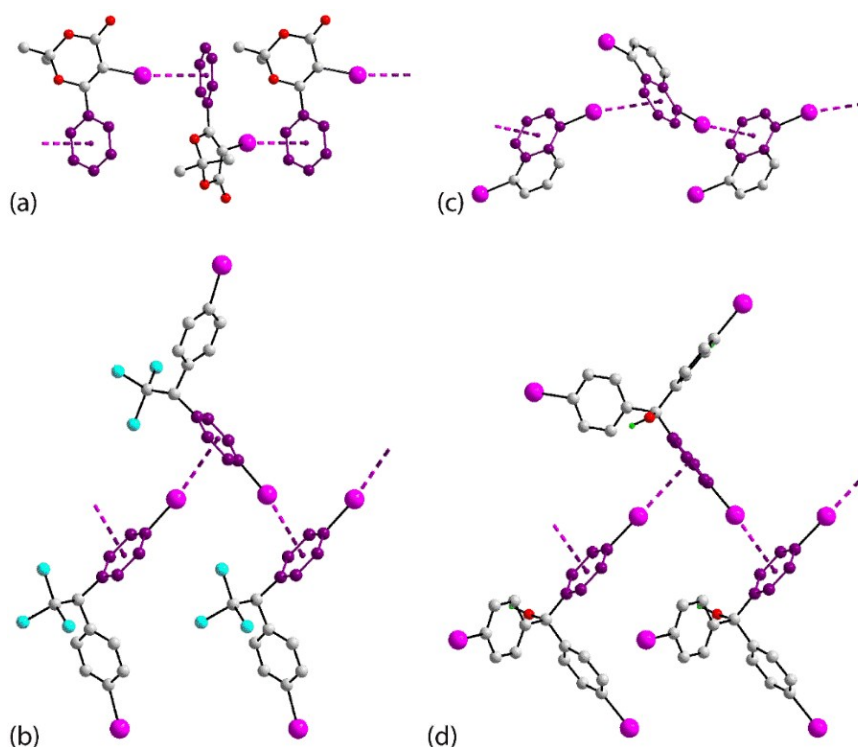
## Helical, one-dimensional supramolecular chains sustained by C–I $\cdots\pi$ (arene) interactions

In this section, the most represented class of supramolecular chains sustained by C–I $\cdots\pi$ (arene) interactions are summarised, namely those with helical topology. There are 36 examples, Fig. 11, of molecules having the sole iodide atom present in their molecular formula forming the contact: **113**,<sup>176</sup> **114**,<sup>177</sup> **115**,<sup>178</sup> **116**,<sup>179</sup> **117**,<sup>180</sup> **118**,<sup>181</sup> **119**,<sup>182</sup> **120**,<sup>183</sup> **121**,<sup>184</sup> **122**,<sup>185</sup> **123**,<sup>186</sup> **124**,<sup>187</sup> **125**,<sup>188</sup> **126**,<sup>189</sup> **127**,<sup>190</sup> **128**,<sup>191</sup> **129**,<sup>192</sup> **130**,<sup>193</sup> **131**,<sup>194</sup> **132**,<sup>195</sup> **133**,<sup>196</sup> **134**,<sup>197</sup> **135**,<sup>198</sup> **136**,<sup>199</sup> **137**,<sup>200</sup> **138**,<sup>201</sup> **139**,<sup>202</sup> **140**,<sup>203</sup> **141**,<sup>204</sup> **142**,<sup>205</sup> **143**,<sup>206</sup> **144**,<sup>207</sup> **145**,<sup>208</sup> **146**,<sup>209</sup> **147**,<sup>210</sup> and **148**.<sup>211</sup> Two representative examples, namely for the DDT (dichlorodiphenyltrichloroethane) analogue, **126**,<sup>189</sup> and **127**,<sup>190</sup> are shown in Figs 12(a) and (b), respectively; the latter is notable for having a –CF<sub>3</sub> group but no C–Cl $\cdots\pi$ (arene) interactions are noted in the crystal. The common feature of all of the helical chains is that they are propagated by 2<sub>1</sub>-screw symmetry in their crystals, see ESI Table 5. Further, except for **114**,<sup>177</sup> **121**,<sup>184</sup> and **129**,<sup>192</sup> each features a single molecule in the crystallographic asymmetric unit. In **114**,<sup>177</sup> each of the two molecules in the asymmetric unit form helical chains. Highlighting the pervasive nature of helical chain formation, in each of **121**,<sup>184</sup> and **129**,<sup>192</sup> one of the independent molecules forms a helical chain and so does the second but, with geometric parameters outside the search limits for delocalised C–I $\cdots\pi$ (arene) interactions, ESI Table S5.



**Fig. 11** Chemical diagrams for molecules **113-148** which form a helical, one-dimensional chain in their crystals sustained by a C–I $\cdots\pi$ (arene) interactions.

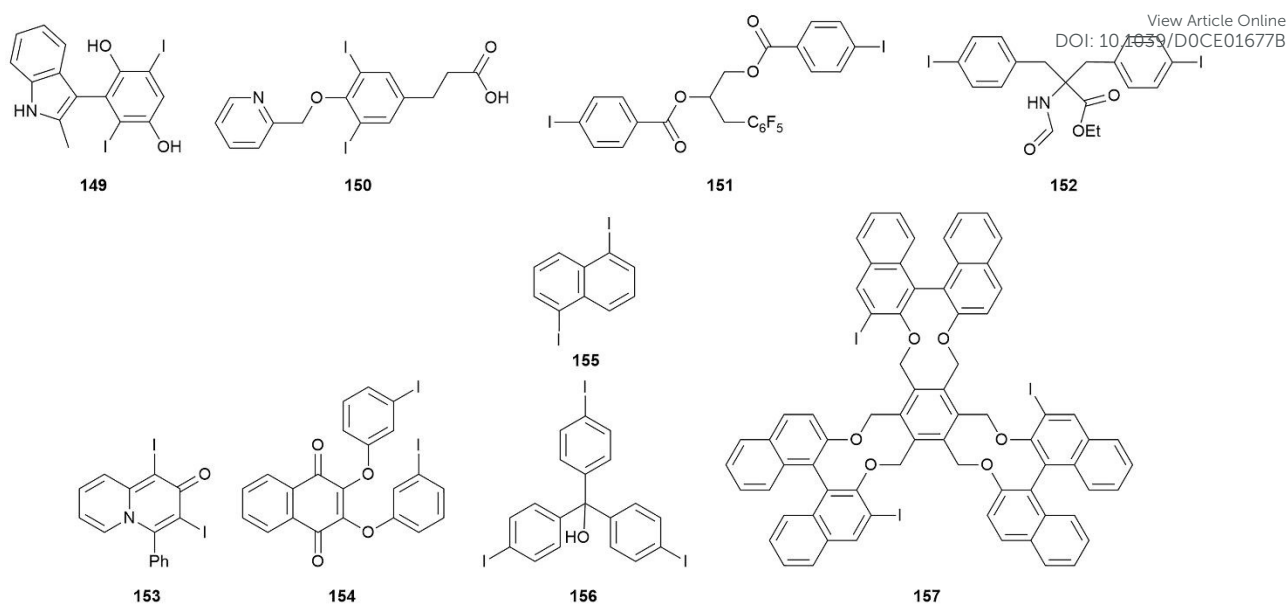




**Fig. 12** Supramolecular aggregation in helical, one-dimensional chains sustained by C–I $\cdots\pi$ (arene) interactions: (a) **126**, (b) **127**, (c) **155** and (d) **156**.

Complementing 37 examples in this category with a single iodide substituent, are seven molecules with two iodide substituents, *i.e.* **149**,<sup>212</sup> **150**,<sup>213</sup> **151**,<sup>214</sup> **152**,<sup>215</sup> **153**,<sup>216</sup> **154**<sup>217</sup> and **155**,<sup>218</sup> and two with three, *i.e.* **156**<sup>48</sup> and **157**,<sup>219</sup> see Fig. 13 for chemical diagrams. Representative aggregation patterns are illustrated for **155**<sup>218</sup> and **156**<sup>48</sup> in Figs 12(c) and (d), respectively. In all crystals but **157**,<sup>219</sup> one molecule comprises the asymmetric unit; in the extraordinary case, two molecules comprise the asymmetric unit and each forms a helical chain in the crystal. All helical chains are propagated by 2<sub>1</sub>-screw symmetry and each molecule accepts and donates one C–I $\cdots\pi$ (arene) interaction. A solvated form of **156**<sup>48</sup> also features in this survey, namely in **110**.<sup>48</sup> In this case, a zig-zag supramolecular chain is formed.

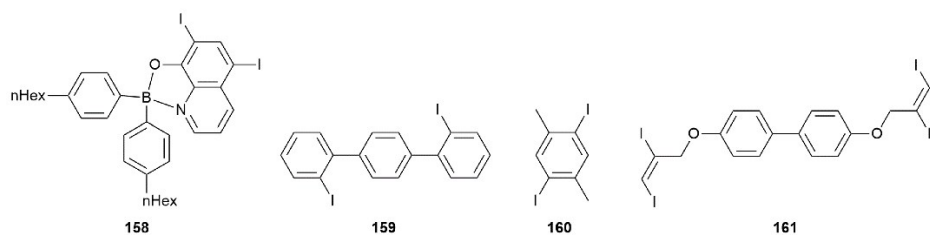




**Fig. 13** Chemical diagrams for molecules **149-157**, having multiple iodide substituents, which form a helical, one-dimensional chain in their crystals sustained by a C–I $\cdots\pi$ (arene) interactions.

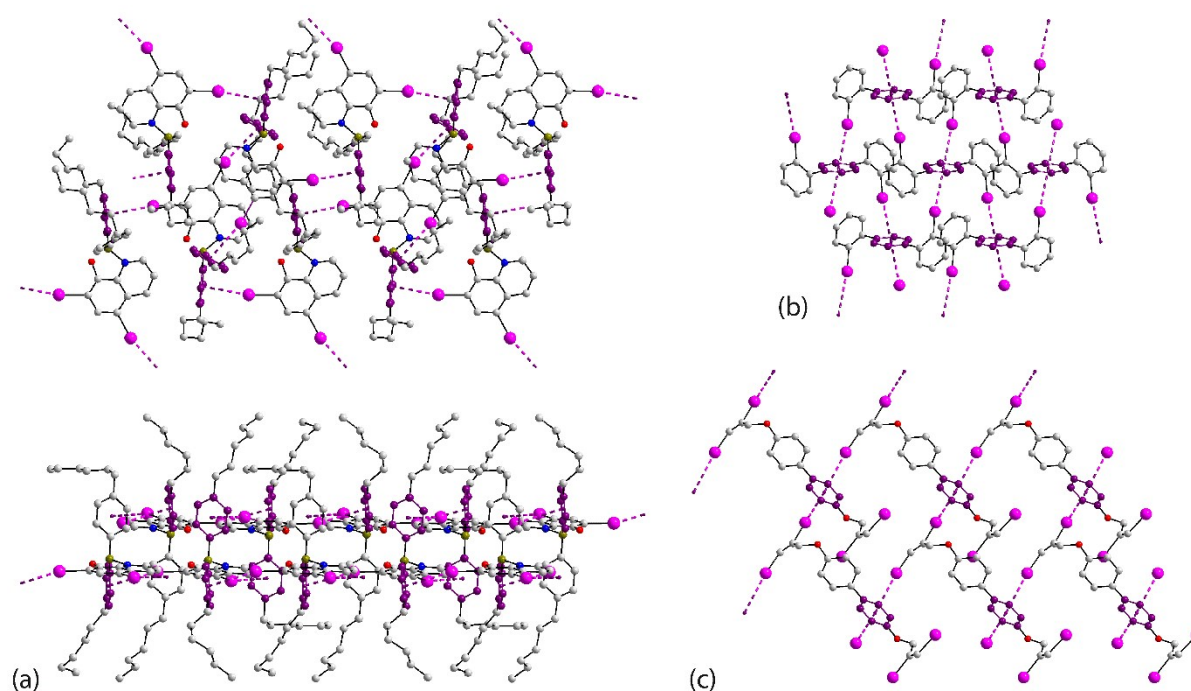
### Two-dimensional aggregates sustained by a C–I $\cdots\pi$ (arene) interactions

There are four crystals in this category, three having two iodide substituents in their molecular formula, *i.e.* **158**,<sup>220</sup> **159**<sup>221</sup> and **160**,<sup>222</sup> and one having four substituents, namely **161**,<sup>223</sup> see Fig. 14 for chemical diagrams and ESI Table 6 for further details.



**Fig. 14** Chemical diagrams for molecules **158-161** which form two-dimensional arrays in their crystals sustained by C–I $\cdots\pi$ (arene) interactions.

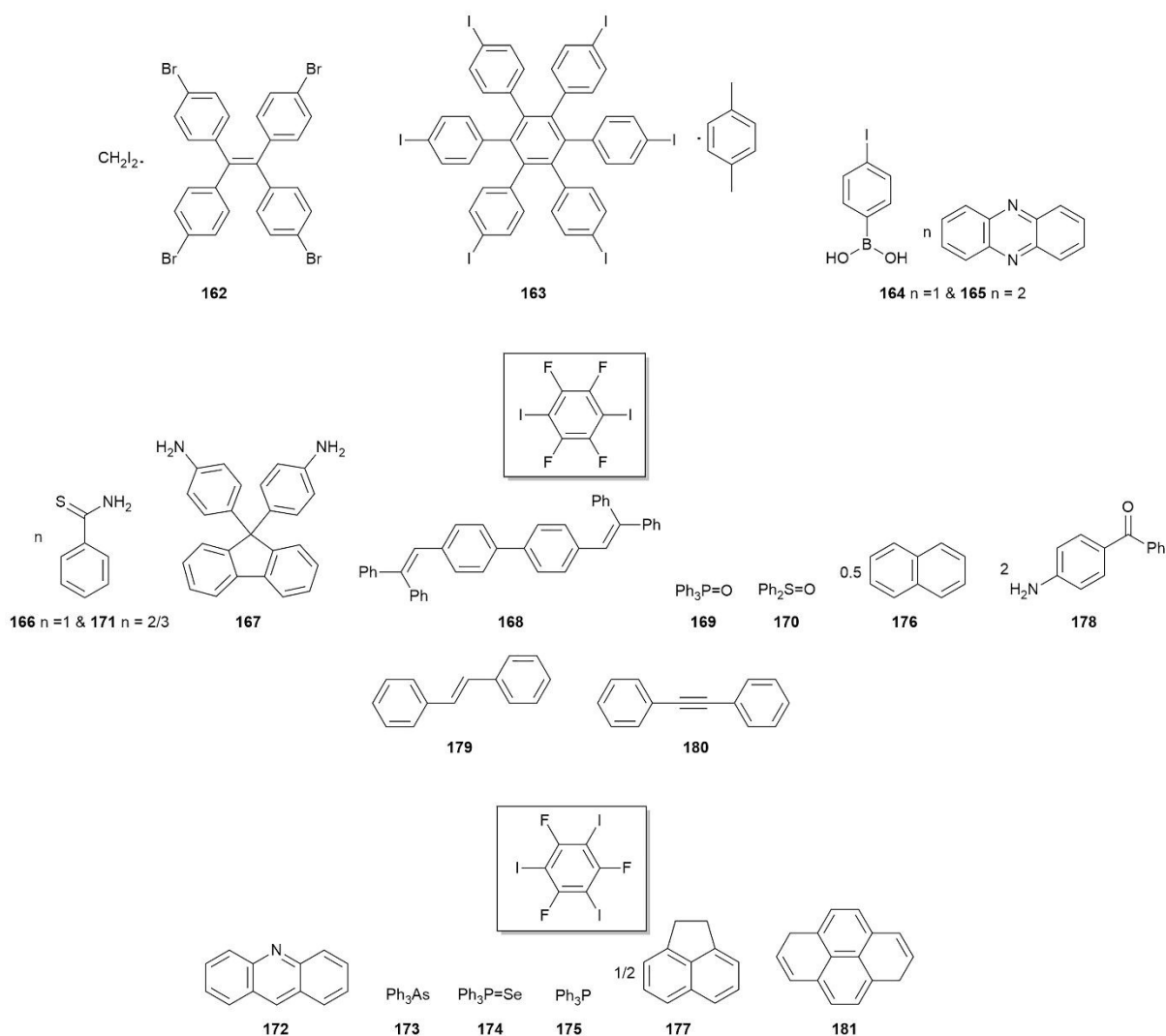
Two distinct structural motifs are observed for the compounds with two iodide atoms. The first of these, illustrated in the two views of Fig. 15(a), is found in the crystal of **158**,<sup>220</sup> where two molecules comprise the asymmetric unit. Each of the molecules accepts and donates two C–I $\cdots\pi$ (arene) interactions which extend laterally to form a two-dimensional array, two molecules thick. In the second motif, found in each of **159**<sup>221</sup> and **160**,<sup>222</sup> one arene ring, located about a centre of inversion, accepts two contacts, one to either side, and each of the iodide atoms participates in a C–I $\cdots\pi$ (arene) interaction. Again, these extend laterally to form a two-dimensional array as illustrated for **159**<sup>221</sup> in Fig. 15(b). In the tetra-iodide species, **161**,<sup>223</sup> again one ring accepts two C–I $\cdots\pi$ (arene) interactions but only two of the iodide atoms participate in these contacts, giving rise to the array shown in Fig. 15(c).



**Fig. 15** Supramolecular aggregation in two-dimensional arrays sustained by C–I $\cdots\pi$ (arene) interactions: (a) **158** (plan and side-on views), (b) **159** and (c) **161**.

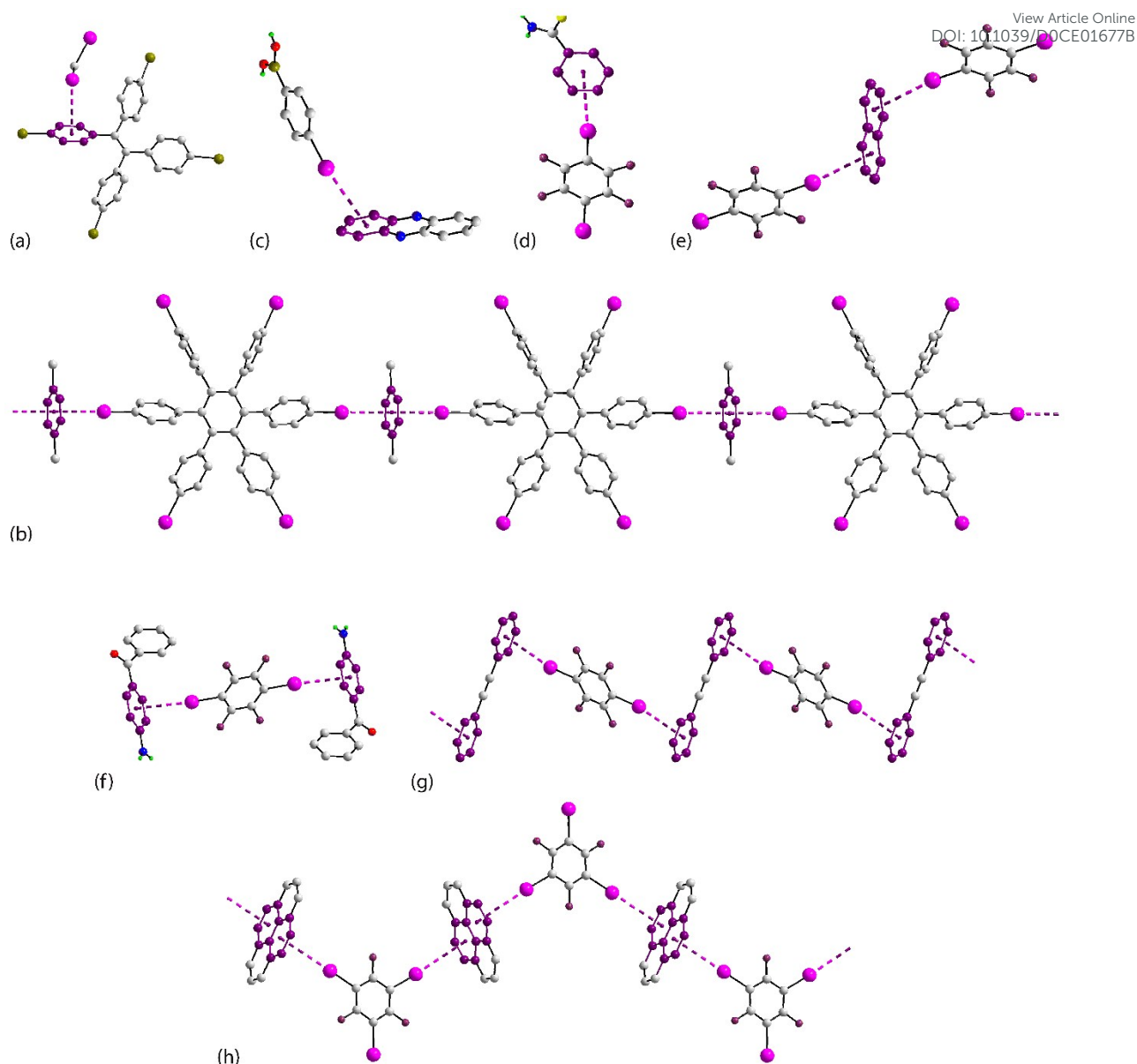
#### Aggregates sustained by C–I $\cdots\pi$ (arene) interactions in multi-component crystals

For completeness, in this section, multi-component crystals found to present C–I... $\pi$ (arene) interactions between the different constituents in their crystals are described. There are two examples of solvates, namely **162**<sup>224</sup> and **163**;<sup>225</sup> see Fig. 16 for chemical diagrams and ESI Table 7 for details. In the former, a 2:3 solvate, an iodide atom of CH<sub>2</sub>I<sub>2</sub> interacts with a ring of the tetra-brominated species to form the two-molecule aggregate shown in Fig. 17(a); no C–Br... $\pi$ (arene) interactions are noted in the molecular packing. In the second solvate, **163**,<sup>225</sup> each of the constituents is disposed about a 2-fold axis of symmetry and line up along this axis to form a twisted chain, Fig. 17(b). The arene rings accept two C–I... $\pi$ (arene) interactions but only two of the six iodide atoms in the hexa-iodide species are involved in such contacts.



**Fig. 16** Chemical diagrams for the interacting constituents connected by C–I... $\pi$ (arene) interactions in multi-component crystals **162–181**. Crystals of **166–171**, **176** and **178–180** are co-crystals with 1,4-C<sub>6</sub>F<sub>4</sub>I<sub>2</sub>, and crystals of **172–175**, **177** and **181** are co-crystals with 1,3,5-C<sub>6</sub>F<sub>3</sub>I<sub>3</sub>.

The remaining structures to be described fall under the aegis of co-crystals. The co-formers of co-crystals **164**,<sup>226</sup> **165**,<sup>226</sup> **166**,<sup>227</sup> **167**,<sup>228</sup> **168**,<sup>228</sup> **169**,<sup>229</sup> **170**,<sup>230</sup> **171**,<sup>227</sup> **172**,<sup>231</sup> **173**,<sup>232</sup> **174**,<sup>233</sup> and **175**,<sup>232</sup> Fig. 16, adopt a common, zero-dimensional motif comprising two different molecules connected by a single C–I... $\pi$ (arene) interaction. With the exceptions of **165**,<sup>226</sup> Fig. 17(c), which is a 1 (iodide-containing species):2 co-crystal monohydrate, and **171**,<sup>227</sup> Fig. 17(d), a 3:2 co-crystal, the remaining examples are solvent-free, 1:1 co-crystals, ESI Table 8. Interestingly, the aggregates formed in **165**<sup>226</sup> and **171**<sup>227</sup> are, to a first approximation, the same as those aggregates found in the pure 1:1 co-crystals containing the same species, *i.e.* **164**<sup>226</sup> and **166**,<sup>227</sup> respectively. Further, in its pure form the iodide-containing co-former of each of **164**<sup>226</sup> and **165**<sup>226</sup> forms a single C–I... $\pi$ (arene) interaction between a pair of independent molecules to form a two-molecule aggregate, see **2**.<sup>71</sup> Of the aforementioned di- and tri-iodide co-crystals, only in **167**<sup>228</sup> is there a suggestion of an additional C–I... $\pi$ (arene) interaction, outside the specified search criteria for delocalised interactions, leading to a higher aggregation pattern, in this case, a linear chain, see ESI Table 8 for details.



**Fig. 17** Supramolecular aggregation sustained by C–I $\cdots\pi$ (arene) interactions in multi-component crystals: (a) **162**, (b) **163**, (c) **165**, (d) **171**, (e) **176**, (f) **178**, (g) **180** and (h) **181**.

Related zero-dimensional aggregates are noted in the crystals of **176**,<sup>234</sup> Fig. 18(e), and **177**.<sup>235</sup> In these instances, two rings of the accepting molecules connect to the co-crystal co-formers, leading to three-molecule aggregates. In **176**,<sup>234</sup> the naphthalene molecule is disposed about a centre of inversion, and if there search criteria were relaxed, each ring effectively connects to two different 1,4-C<sub>6</sub>F<sub>4</sub>I<sub>2</sub> molecules with the result being the formation of a

supramolecular tape, see ESI Table 8. In **177**,<sup>235</sup> the asymmetric unit comprises four independent, donating 1,3,5-C<sub>6</sub>F<sub>3</sub>I<sub>3</sub> molecules and two independent, accepting 1,2-dihydroacenaphthylene molecules with the result that two independent, three-molecule aggregates are formed. If additional C–I⋯π(arene) interactions outside the search criteria were taken into consideration, a second iodide atom in each case participates in a C–I⋯π(arene) interaction so that each ring accepts two contacts. In this scenario, the result is a two-dimensional array with an undulating topology, see ESI Table 8.

In the remaining aggregates to be described, the donating molecules form bridging interactions to arene rings. The chemical diagrams for **178**,<sup>236</sup> **179**,<sup>237</sup> **180**<sup>237</sup> and **181**<sup>238</sup> are given in Fig. 16. A three-molecule is seen in the crystal of **178**,<sup>236</sup> Fig. 17(f), where the 1,4-C<sub>6</sub>F<sub>4</sub>I<sub>2</sub> molecule is disposed about a centre of inversion. In each of **179**<sup>237</sup> and **180**,<sup>237</sup> Fig. 17(g), the co-formers are disposed about centre of inversion and the resultant linear, supramolecular chain has a step-ladder topology. Finally, in **181**,<sup>238</sup> where the 1,3,5-C<sub>6</sub>F<sub>3</sub>I<sub>3</sub> molecule has 2-fold symmetry and the pyrene molecule is situated about a centre of inversion, a zig-zag, supramolecular chain results as only the symmetry-related iodide atoms form C–I⋯π(arene) interactions, Fig. 17(h).

## Overview

The results of a survey of the crystallographic literature seeking the presence of delocalised C–I⋯π(arene) interactions has been presented. A total of 181 crystals were found to feature such interactions with the distance between an iodide atom and the ring centroid (Cg) of an arene ring it approaches being less than 3.88 Å and with the C–I⋯Cg angle lying in the range 160–180°. The identified contacts are operating independently of any other obvious atom-to-atom contacts. There were 77 zero-dimensional, supramolecular aggregates sustained by delocalised C–I⋯π(arene) interactions, 100 supramolecular chains and four two-dimensional arrays.

Among the zero-dimensional aggregates, the maximum number of molecules comprising the aggregate was two. In nearly 75% of zero-dimensional aggregates, there were two delocalised C–I $\cdots\pi$ (arene) interactions between the molecules. By contrast, in the overwhelming majority of one-dimensional chains there was, on average, one C–I $\cdots\pi$ (arene) interaction per repeat unit, there being only two exceptions, *i.e.* **85**<sup>150</sup> and **109**,<sup>173</sup> out of 100 examples. In keeping with the delocalised nature of the C–I $\cdots\pi$ (arene) interactions, there were no bifurcated C–I $\cdots\pi$ (arene) interactions. In terms of the accepting arene rings, in most cases, the ring accepted a single C–I $\cdots\pi$ (arene) interaction only, there being only four instances where the ring accepted two contacts, *i.e.* in the two-dimensional arrays of **159**,<sup>221</sup> **160**<sup>222</sup> and **161**,<sup>223</sup> and in the one-dimensional chain of **163**.<sup>225</sup>

Allowing for multiple aggregates in the surveyed crystals, there are 199 independent C–I $\cdots\pi$ (arene) interactions. The range of  $d$  values was 3.272(5) Å in **163**<sup>225</sup> to 3.8785(7) Å in **49**.<sup>118</sup> The average value of  $d$  was 3.674 Å and median value, very similar at 3.678 Å. Owing to the intention to evaluate delocalised C–I $\cdots\pi$ (arene) interactions only, the values of  $\theta$  were limited to lie between 160 and 180°. This constraint notwithstanding, the average value of  $\theta$  was 166.9° and median value 166.6°. It is noted the shortest value of  $d$  in the surveyed crystals is associated with the widest angle, *i.e.* 180° in **49**.<sup>118</sup> However, a plot of  $\theta$  versus  $d$ , see ESI Fig. 1, showed this structure was in fact an outlier and that no correlation between  $\theta$  versus  $d$  is evident. This lack of correlation is well established for non-covalent interactions<sup>239–241</sup> and has been highlighted in several instances in the present review for parameters within the same crystal, *e.g.* **20**,<sup>89</sup> **50**,<sup>119</sup> **79**,<sup>144</sup> *etc.*; also, see below. The absence of a correlation between  $\theta$  versus  $d$  generally relates to a number of chemical factors such as different electronic effects impacting upon both the iodide donor and accepting arene ring, steric hindrance, competing or even complementary intermolecular interactions, *etc.*<sup>239–243</sup> In addition, the crystalline manifold and the conditions under which the crystallographic experiment is conducted, such



as temperature, can have an impact upon the geometric parameters defining weak intermolecular interactions.<sup>244,245</sup> In this context and the above notwithstanding, it is worth mentioning a room temperature, variable-pressure study<sup>246</sup> of previously described **19**,<sup>88</sup> which is a centrosymmetric, two-molecule aggregate. Under ambient conditions,  $d = 3.563(2)$  Å and  $\theta = 164.78(14)^\circ$  but when the pressure was increased to 4.88 GPa,  $d$  reduced to 3.215(3) Å with an accompanying straightening of the  $\theta$  angle to  $169.3(3)^\circ$ . Certainly, more systematic crystallographic studies in this area are warranted, especially under non-ambient conditions.

### Likelihood of formation

Attention is now directed towards evaluating the propensity for the formation of C–I $\cdots\pi$ (arene) interactions. In the present survey, 181 crystals were identified as having delocalised C–I $\cdots\pi$ (arene) interactions. An additional search of the CSD<sup>64</sup> was conducted, employing the same restrictions as outlined above in the *Methods* section, for every crystal with a C–I bond and an arene ring. This retrieved over 4200 hits (no sorting) implying just over 4% of all possible crystals where these interactions can form actually feature delocalised C–I $\cdots\pi$ (arene) interactions. When the range of  $\theta$  angle was expanded to 90–180°, allowing for the possibility of both semi-localised and localised C–I $\cdots\pi$ (arene) interactions, 645 hits (no sorting) were retrieved corresponding to a considerably greater adoption rate of 15%. Either percentage adoption rate does not suggest a particularly great prevalence of this mode of association between molecules. The 4% adoption rate for delocalised C–I $\cdots\pi$ (arene) interactions may be compared with 6% adoption of delocalised M(lone-pair) $\cdots\pi$ (arene) interactions in antimony<sup>241</sup> and in tellurium<sup>240</sup> crystals capable of forming such interactions.

Several additional surveys of the crystallographic literature were conducted employing the CSD.<sup>64</sup> These included a search for structures with the identical molecular formula as for



the iodide-containing molecule of each of **1-181** to ascertain whether specific molecules exhibit a propensity to form C–I $\cdots\pi$ (arene) interactions. Also, a search was made for congeners, *i.e.* analogous molecules where the iodide atom(s) of **1-181** were substituted for a bromide, chloride and fluoride atom(s). Unlike the CSD search leading to the identification of **1-181**, no restrictions were applied to the angle  $\theta$  in the searches for congeners; the other criteria were retained. The results of the additional CSD searches are summarised in ESI Table 9.

The first search for analogues among the 181 compounds, revealed the presence of two polymorphs. For **99**<sup>162</sup> (orthorhombic: *Pbca* and  $Z' = 1$ ), its polymorph (monoclinic: *C2/c* and  $Z' = 0.5$ ) exhibited no equivalent C–I $\cdots\pi$ (arene) interactions, and the same observation is true for **155** (orthorhombic: *P2<sub>1</sub>2<sub>1</sub>2<sub>1</sub>* and  $Z' = 1$ )<sup>220</sup> and its polymorph (*P2<sub>1</sub>/n* and  $Z' = 1$ )<sup>247</sup>. The most represented of the 181 compounds covered in this survey is 4-iodophenylboronic acid found in **2**,<sup>71</sup> and in co-crystals **164** and **165**<sup>226</sup> all featuring C–I $\cdots\pi$ (arene) interactions. However, when 4-iodophenylboronic acid is co-crystallised with 4,4'-bipyridine, as a monohydrate, 1.5 equivalents of *trans*-1,2-bis(4-pyridyl)ethene, 0.5 equivalent of 4,7-phenanthroline,<sup>226</sup> isonicotinamide, nicotinamide<sup>248</sup> and 1,3-dimethyl-3,7-dihydro-1H-purine-2,6-dione,<sup>249</sup> no C–I $\cdots\pi$ (arene) interactions were observed. The tri-iodide species, 1,3,5-triethyl-2,4,6-tris((4-iodophenoxy)methyl)benzene, **15**,<sup>84</sup> appears in three other crystals, namely in the *m*-xylene solvate, **86**,<sup>151</sup> and in the chloroform and 1,2-dichloroethane solvates.<sup>151</sup> In the latter two examples, C–I $\cdots\pi$ (arene) interactions are apparent but with the  $\theta$  angles deviating by a several degrees from 160°. Three crystals are also known to contain tris(4-iodophenyl)methanol, *i.e.* the dichloromethane solvate, **110**,<sup>57</sup> the unsolvated form, **156**,<sup>57</sup> each of which are described herein but, when this molecule is co-crystallised as the benzene hemi-solvate,<sup>57</sup> no C–I $\cdots\pi$ (arene) interaction is noted. Three molecules each feature in two structures included in this survey, *i.e.* **168**<sup>85</sup> & **87**,<sup>76</sup> **58** & **59**,<sup>127</sup> and **166** & **171**,<sup>227</sup> with no additional literature counterparts. The 1:1 co-crystal formed with co-formers 1,1'-ethyne-

1,2-diiodobenzene and 1,2,4,5-tetrafluoro-3,6-di-iodobenzene, **180**,<sup>237</sup> assemble into a linear chain *via* C–I $\cdots\pi$ (arene) interactions. The 1:2 co-crystal is also known,<sup>237</sup> and related linear chains are also sustained by C–I $\cdots\pi$ (arene) interactions but, with  $\theta$  angles less than 160°. Finally, when **29**<sup>98</sup> is co-crystallised with chloroform,<sup>98</sup> the C–I $\cdots\pi$ (arene) interaction no longer persists. A similar observation is noted when **129**<sup>192</sup> is co-crystallised with 4,4'-bipyridine,<sup>192</sup> and when **143**<sup>205</sup> is co-crystallised with 3,5-dinitrobenzoic acid.<sup>250</sup> In summary, the analysis of molecules featured in this survey indicates there is no inherent likelihood for the formation of C–I $\cdots\pi$ (arene) interactions in crystals containing any of the iodide molecules of **1-181**.

A survey of X = bromide, chloride and fluoride congeners of **1-181** was also conducted with the results summarised in Table 1 and with further complete details included in ESI Table 9. The results may be considered in three categories: i) where the iodide-containing compound is different to all congeners in terms of the formation of C–X $\cdots\pi$ (arene) interactions in their crystals, ii) there are some structural similarities among the congeners and iii) the congeners form isostructural series. Congeners with isostructural relationships are highlighted with a cyan background in Table 1.

The first category involves crystals **1**,<sup>70</sup> **4**,<sup>73</sup> **48**,<sup>117</sup> **51**,<sup>120</sup> **105**,<sup>169</sup> **155**,<sup>205</sup> **160**,<sup>222</sup> **164**<sup>226</sup> and **181**.<sup>238</sup> Of the nine crystals, five have congeners having C–X $\cdots\pi$ (arene) interactions and of these, congeners of **4**,<sup>73</sup> *i.e.* bromide,<sup>253</sup> chloride<sup>254</sup> but, not fluoride<sup>255</sup> have C–X $\cdots\pi$ (arene) interactions close to being classified as delocalised in terms of this survey. For congeners of **51**,<sup>120</sup> *i.e.* chloride,<sup>256</sup> and **181**,<sup>238</sup> *i.e.* bromide<sup>238</sup> and fluoride,<sup>272</sup> side-on C–X $\cdots\pi$ (arene) interactions occur in their crystals. The bromide congener of **160**,<sup>222</sup> crystallises as two monoclinic polymorphs<sup>269,270</sup> with a delocalised C–Br $\cdots\pi$ (arene) interaction occurring in the polymorph with the molecule being disposed about a centre of inversion.<sup>269</sup> The most studied group of congeners are for crystal **1** for which two polymorphs are known for each of the bromide, chloride and fluoride analogues with each series being isostructural but not

isostructural with **1**.<sup>70,251,252</sup> While the monoclinic ( $P2_1/c$ ) polymorphs do not exhibit C–X $\cdots\pi$ (arene) interactions, the triclinic ( $P\bar{1}$ ) series does exhibit side-on C–X $\cdots\pi$ (arene) interactions; the participating fluoride atom in the fluoride analogue is bifurcated.<sup>70,251,252</sup> No C–X $\cdots\pi$ (arene) interactions are noted in the crystals of the congeners known for **48**,<sup>117</sup> **105**,<sup>169</sup> **155**<sup>205</sup> and **164**,<sup>226</sup> Table 1.

The second category of crystals comprises six examples. Here, there is a combination of isostructural and non-isostructural relationships. For **80**,<sup>145</sup> the bromide and chloride congeners are isostructural but, that the fluoride congener is not.<sup>145</sup> In spite of the isostructural relationship, no C–X $\cdots\pi$ (arene) interactions are apparent in the respective crystals,<sup>145</sup> suggesting the C–I $\cdots\pi$ (arene) interaction in **80** is not structure-directing; no C–F $\cdots\pi$ (arene) interaction is noted in the fluoride analogue.<sup>145</sup> This is the exceptional observation within this category. Thus, for **36**,<sup>105</sup> **71**,<sup>138</sup> **127**,<sup>190</sup> **130**,<sup>193</sup> and **139**,<sup>202</sup> the isostructural bromide analogues exhibit comparable or close to delocalised C–Br $\cdots\pi$ (arene) interactions, respectively.<sup>105,138,258,193,264</sup> Each of these iodide-containing molecules also has a chloride congener, respectively.<sup>104,138,259,260,193,250</sup> While a delocalised C–Cl $\cdots\pi$ (arene) interaction is apparent in the congener of **127**,<sup>190</sup> the only other congener to exhibit a C–Cl $\cdots\pi$ (arene) interaction is that of **36**,<sup>105</sup> *i.e.* a side-on contact. No C–F $\cdots\pi$ (arene) interactions were noted in four of the known fluoride congeners.<sup>105,145,193,250</sup> There are two polymorphs known for the fluoride congener of **127**,<sup>190</sup> namely two monoclinic ( $P2_1/c$ ) polymorphs. In the  $Z' = 4$  form,<sup>261</sup> a two-molecule aggregate formed between two of the independent molecules is sustained by a close to delocalised C–F $\cdots\pi$ (arene) interaction with many other, side-on delocalised C–F $\cdots\pi$ (arene) interactions being apparent. In the  $Z' = 1$  form,<sup>261</sup> a pair of rather long, side-on C–F $\cdots\pi$ (arene) interactions sustain a two-molecule aggregate.

In the third and final category, only isostructural relationships between the congeners are apparent. There are eleven series in this category, with the iodide-congeners being **15**,<sup>84</sup>

**37**,<sup>106</sup> **90**,<sup>154</sup> **134**,<sup>197</sup> **135**,<sup>198</sup> **140**,<sup>203</sup> **143**,<sup>205</sup> **156**,<sup>57</sup> **159**,<sup>221</sup> **165**<sup>226</sup> and **179**.<sup>237</sup> With the exception

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of the fluoride congener of **179**,<sup>237</sup> all of the known congeners exhibit delocalised or close to delocalised C–X $\cdots\pi$ (arene) interactions giving rise to analogous supramolecular aggregates as might be expected from the isostructural relationships, see Table 1 for details. The exceptional structure is the fluoride congener of **179**,<sup>237</sup> where side-on C–F $\cdots\pi$ (arene) interactions lead to a linear chain of alternating co-formers.

Table 1 Summary of data for analogues and congeners of **1-181**. The REFCODES highlighted with a cyan background represent isostructural crystals within each entry.

Compound	Br-analogue/REFCODE	Cl-analogue/REFCODE	F-analogue/REFCODE
<b>1 POPKAI</b> <sup>70</sup>	Hydroxy(3-iodophenyl)acetic acid: <i>two-molecule aggregate via a single interaction</i>		
	POPJEL <sup>70</sup>	FIZPEL02 <sup>70</sup>	WESBIF01 <sup>70</sup>
	no interaction	no interaction	no interaction
	POPJEL01 <sup>70</sup>	FIZPEL <sup>251</sup>	WESBIF <sup>252</sup>
$d = 3.521(3) \text{ \AA}, \theta = 165.0(2)^\circ$	$d = 3.7763(19) \text{ \AA}, \theta = 112.95(13)^\circ$	$3.8225(10) \text{ \AA}, \theta = 110.20(7)^\circ$	$3.5961(12) \text{ \AA}, 132.46(7)^\circ$
			$3.7691(12) \text{ \AA}, 78.84(8)^\circ$
<b>4 SAJPIF</b> <sup>73</sup>	4-Iodophenylboronic acid hemihydrate: <i>two-molecule aggregate via a single interaction</i>		
	QEVSES <sup>253</sup>	DUJKAV <sup>254</sup>	PURBAH <sup>255</sup>
$d = 3.5945(18) \text{ \AA}, \theta = 160.90(11)^\circ$	$d = 3.533(3) \text{ \AA}, \theta = 142.0(2)^\circ$	$d = 3.6417(15) \text{ \AA}, \theta = 139.78(8)^\circ$	no interaction
<b>15 YASQIU03</b> <sup>84</sup>	1,3,5-Triethyl-2,4,6-tris((4-iodophenoxy)methyl)benzene: <i>two-molecule aggregate via a single interaction</i>		
	<b>YASTOD</b> <sup>84</sup>	<b>YASXIB01</b> <sup>151</sup>	—
$d = 3.657(2) \text{ \AA}, \theta = 160.11(15)^\circ$	$d = 3.5123(17) \text{ \AA}, \theta = 157.64(14)^\circ$	$d = 3.5139(9) \text{ \AA}, \theta = 159.70(8)^\circ$	
$d = 3.535(2) \text{ \AA}, \theta = 152.9(2)^\circ$	$d = 3.6204(17) \text{ \AA}, \theta = 156.04(14)^\circ$	$d = 3.6901(9) \text{ \AA}, \theta = 155.59(8)^\circ$	
<b>36 GOYMAL</b> <sup>105</sup>	9-(5-Iodopyridin-3-yl)-9H-carbazole: <i>centrosymmetric dimer</i>		

	<b>GOYLUE</b> <sup>105</sup>	GOYLIS <sup>105</sup>	GOYMEP <sup>105</sup>
$d = 3.741(3) \text{ \AA}, \theta = 163.2(2)^\circ$	$d = 3.646(3) \text{ \AA}, \theta = 149.74(17)^\circ$	$d = 3.6753(12) \text{ \AA}, \theta = 72.73(8)^\circ$	no interaction
$d = 3.635(3) \text{ \AA}, \theta = 145.6(2)^\circ$	$d = 3.738(3) \text{ \AA}, \theta = 162.96(17)^\circ$		
<b>37 NICRAU</b> <sup>106</sup>	2-Bromo-10-(5-bromo-2-iodophenyl)-9-phenylanthracene: <i>centrosymmetric dimer</i>		
	<b>NICREY</b> <sup>106</sup>	<b>KETXOY</b> <sup>106</sup>	—
$d = 3.762(2) \text{ \AA}, \theta = 166.46(13)^\circ$	$d = 3.4926(17) \text{ \AA}, \theta = 150.20(13)^\circ$	$d = 3.4912(17) \text{ \AA}, \theta = 150.23(13)^\circ$	
<b>48 DEGWUJ</b> <sup>117</sup>	2-Iodo-4-(1-(3,5,5,8,8-pentamethyl-5,6,7,8-tetrahydronaphthalen-2-yl)vinyl)benzoic acid: <i>centrosymmetric dimer</i>		
	DEGWOD <sup>117</sup>	DEGWIX <sup>117</sup>	—
$d = 3.862(2) \text{ \AA}, \theta = 163.38(15)^\circ$	no interaction	no interaction	
<b>51 VIKHOP</b> <sup>120</sup>	bis(Iodomethyl)phenylphosphine oxide: <i>centrosymmetric dimer</i>		
	—	ODUMUX <sup>256</sup>	—
$d = 3.6983(19) \text{ \AA}, \theta = 170.77(12)^\circ$		$d = 3.447(3) \text{ \AA}, \theta = 132.84(19)^\circ$	
<b>71 TUFXEZ</b> <sup>138</sup>	7-Iodo-7-phenylbicyclo[2.2.1]heptane: <i>linear chain</i>		
	<b>TUFXID</b> <sup>138</sup>	TUFXOJ <sup>138</sup>	—
$d = 3.681(5) \text{ \AA}, \theta = 178.27(14)^\circ$	$d = 3.589(3) \text{ \AA}, \theta = 176.62(9)^\circ$	no interaction	
<b>80 UVECEF</b> <sup>145</sup>	1,1'-Pyrene-1,3-diylbis(2-iodoethanone): <i>linear chain</i>		
	<b>UVECAB</b> <sup>145</sup>	<b>UVEBUU</b> <sup>145</sup>	UVEBOO <sup>145</sup>

$d = 3.647(3) \text{ \AA}, \theta = 165.41(19)^\circ$	no interaction	no interaction	no interaction
<b>90 FANJOY</b> <sup>154</sup>	4-(4-(Iodo)phenoxy)aniline: <i>zig-zag chain</i>		
	<b>FANYID</b> <sup>154</sup>	<b>FANYEX</b> <sup>154</sup>	—
$d = 3.5100(16) \text{ \AA}, \theta = 171.39(12)^\circ$	$d = 3.4299(10) \text{ \AA}, \theta = 169.66(7)^\circ$	$d = 3.4288(11) \text{ \AA}, \theta = 168.01(7)^\circ$	
<b>105 QOMYOG</b> <sup>169</sup>	1,1,2,2-Tetraphenyl-3,8-diiodocyclobuta(b)naphthalene: <i>zig-zag chain</i>		
	QOMYIA <sup>169</sup>	ZIVLIZ <sup>257</sup>	—
$d = 3.577(3) \text{ \AA}, \theta = 170.81(13)^\circ$	no interaction	no interaction	
<b>127 ZZZQAC01</b> <sup>190</sup>	1,1,1-Trichloro-2,2-bis(4-iodophenyl)ethane: <i>helical chain</i>		
	<b>ZZZQUDU01</b> <sup>258</sup>	<b>CPTCET12</b> <sup>259,260</sup>	GOXCUUJ <sup>261</sup>
$d = 3.665(4) \text{ \AA}, \theta = 162.5(3)^\circ$	$d = 3.529(2) \text{ \AA}, \theta = 162.34(18)^\circ$	$d = 3.4487(10) \text{ \AA}, \theta = 161.56(7)^\circ$	$d = 3.413(2) \text{ \AA}, \theta = 159.70(19)^\circ$
			GOXCUU01 <sup>261</sup>
			$d = 3.9303(15) \text{ \AA}, \theta = 83.78(9)^\circ$
<b>130 FOYMIS</b> <sup>193</sup>	2-[(2-Iodophenyl)imino]-2H-1-benzopyran-3-carboxamide: <i>helical chain</i>		
	<b>FOYMAK01</b> <sup>193</sup>	FOYLUD <sup>193</sup>	FOYLIR01 <sup>193</sup>
$d = 3.6899(19) \text{ \AA}, \theta = 166.72(13)^\circ$	$d = 3.683(5) \text{ \AA}, \theta = 166.8(3)^\circ$	no interaction	no interaction
<b>134 TIHJUR</b> <sup>197</sup>	8-Iodo-6-(4-methoxyphenyl)-3-((4-methylphenyl)sulfonyl)-3-azatricyclo[5.4.1.0 <sup>1,5</sup> ]dodec-5-ene: <i>helical chain</i>		
	—	<b>TIHKOM</b> <sup>197</sup>	—

$d = 3.739(4) \text{ \AA}, \theta = 163.9(2)^\circ$		$d = 3.727(3) \text{ \AA}, \theta = 165.7(2)^\circ$	
<b>135 VOJBAY</b> <sup>198</sup>	2-Chloro-4-iodoaniline: <i>helical chain</i>	<b>HUGSAE</b> <sup>262</sup>	<b>WEMDIB</b> <sup>263</sup> —
$d = 3.7399(15) \text{ \AA}, \theta = 171.08(9)^\circ$	no interaction	no interaction	
<b>139 BANWIX</b> <sup>202</sup>	N-(4-Iodophenyl)quinoline-2-carboxamide: <i>helical chain</i>	<b>NAZDOJ</b> <sup>264</sup>	<b>RIXHUD</b> <sup>241</sup> <b>RIXJAL</b> <sup>241</sup>
$d = 3.7804(14) \text{ \AA}, \theta = 171.57(8)^\circ$	$d = 3.6072(13) \text{ \AA}, \theta = 172.46(10)^\circ$	no interaction	no interaction
<b>140 VIZLEW</b> <sup>203</sup>	4-Iodo-N,N'-dimethylbenzamidine: <i>helical chain</i>	<b>VIZLAS</b> <sup>203</sup> —	—
$d = 3.792(3) \text{ \AA}, \theta = 167.48(16)^\circ$	$d = 3.7316(14) \text{ \AA}, \theta = 169.48(9)^\circ$		
<b>143 TITZUS</b> <sup>205</sup>	2-Iodo-N-methylaniline: <i>helical chain</i>	<b>ABRTOL</b> <sup>265</sup> —	—
$d = 3.8232(12) \text{ \AA}, \theta = 165.50(7)^\circ$	$d = 3.83 \text{ \AA}, \theta = 178.9^\circ$		
<b>155 NIFHAM</b> <sup>218</sup>	1,5-Diiodonaphthalene: <i>helical chain</i>	<b>COXLOQ</b> <sup>266</sup> —	<b>DFNAPH10</b> <sup>267</sup>
$d = 3.8680(19) \text{ \AA}, \theta = 166.79(10)^\circ$	no interaction		no interaction



<b>156 GIZTEP</b> <sup>57</sup>	tris(4-Iodophenyl)methanol: <i>helical chain</i>		
	<b>GIZTAL</b> <sup>57</sup>	—	—
$d = 3.6600(18) \text{ \AA}$ , $\theta = 169.77(15)^\circ$	$d = 3.5428(14) \text{ \AA}$ , $\theta = 172.21(11)^\circ$		
<b>159 LITBIA</b> <sup>221</sup>	2,2''-bis(Iodo)-(1,1':4',1'')terphenyl: <i>two-dimensional array</i>		
	<b>PORRAQ</b> <sup>268</sup>	—	—
$d = 3.606(3) \text{ \AA}$ , $\theta = 171.50(16)^\circ$	$d = 3.4877(11) \text{ \AA}$ , $\theta = 166.81(7)^\circ$		
<b>160 IBILEN</b> <sup>222</sup>	1,4-bis(Iodo)-2,5-dimethylbenzene: <i>two-dimensional array</i>		
	JAQJAN01 <sup>269</sup>	—	—
$d = 3.849(3) \text{ \AA}$ , $\theta = 173.66(8)^\circ$	$d = 3.5691(8) \text{ \AA}$ , $\theta = 157.13(5)^\circ$		
	JAQJAN <sup>270</sup>		
	no interaction		
<b>164 RORPEV</b> <sup>226</sup>	(4-Iodophenyl)boronic acid phenazine: <i>two-molecule aggregate via a single interaction</i>		
	—	RORNOD <sup>226</sup>	—
$d = 3.678(2) \text{ \AA}$ , $\theta = 166.45(12)^\circ$	no interaction		
<b>165 RORPAR</b> <sup>226</sup>	(4-Iodophenyl)boronic acid bis(phenazine) monohydrate: <i>two-molecule aggregate via a single interaction</i>		
	<b>RORNUJ</b> <sup>226</sup>	—	—
$d = 3.839(3) \text{ \AA}$ , $\theta = 169.36(10)^\circ$	$d = 3.756(3) \text{ \AA}$ , $\theta = 167.93(13)^\circ$		

**179 GUFNOM**<sup>237</sup> 1,1'-Ethene-1,2-diyl dibenzene 1,2,4,5-tetrafluoro-3,6-di-iodobenzene: *linear chain*

—

—

$d = 3.580(6) \text{ \AA}$ ,  $\theta = 166.7(4)^\circ$

**181 QEVWEW**<sup>238</sup> Pyrene 1,3,5-trifluoro-2,4,6-triiodobenzene: *zig-zag chain*

QEVXOH<sup>238</sup>

—

$d = 3.792(3) \text{ \AA}$ ,  $\theta = 162.86(15)^\circ$

$d = 3.597(4) \text{ \AA}$ ,  $\theta = 88.2(2)^\circ$

**TIJTUB**<sup>271</sup>

$d = 3.635(4) \text{ \AA}$ ,  $\theta = 71.6(2)^\circ$

ZZZGKE01<sup>272</sup>

$d = 3.4918(16) \text{ \AA}$ ,  $\theta = 90.82(11)^\circ$

Also included in Table 1 are the key geometric parameters, *i.e.*  $d$  and  $\theta$ , characterising the specified  $C-X\cdots\pi(\text{arene})$  interactions. As a generalisation, contact distances,  $d$ , decrease in the order  $I > Br > Cl > F$ , in accord with expectation. Also, interactions involving iodide are generally more linear than comparable contacts involving bromide and chloride. While fluoride analogues of **1-181** are known, these rarely follow the same structural behaviour as their higher congeners consistent with the well-documented enigmatic behaviour of fluoride, at least when this relates to participation in supramolecular association.<sup>273</sup>

## Conclusions

In all, 181 crystals were found to exhibit delocalised  $C-I\cdots\pi(\text{arene})$  interactions where the iodide atom sits approximately prime to the ring centroid of an arene ring and operating in isolation of conventional supramolecular synthons such as hydrogen bonding. This form of halogen bonding is shown to stabilise zero- and one-dimensional aggregates and, rarely, two-dimensional arrays. The formation of unaided, delocalised  $C-I\cdots\pi(\text{arene})$  interactions in crystals where they can potentially form is rather low at just over a 4% adoption rate; this number increases to approximately 15% when semi-localised and localised  $C-I\cdots\pi(\text{arene})$  interactions are included. While not negating the role of  $C-I\cdots\pi(\text{arene})$  interactions in specific circumstances, such a low adoption rate indicates a relatively small utility as a widely useful design element in crystal engineering. A systematic survey of the crystallographic literature for congeners of the 181 iodide-compounds suggests delocalised  $C-I\cdots\pi(\text{arene})$  interactions are more prevalent than those involving bromide which in turn are more common than equivalent interactions formed by chloride and certainly more so than involving fluoride. An evaluation of isostructural series of crystals indicates that  $C-I\cdots\pi(\text{arene})$  interactions can be structure directing, especially for  $X = \text{iodide and bromide congeners}$ .

### Conflicts of interest

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There are no conflicts to declare.

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The submission entitled: *"Supramolecular architectures sustained by delocalised C–I... $\pi$ (arene) interactions in molecular crystals and the propensity of their formation"*.

A survey of delocalised C–I... $\pi$ (chelate ring) interactions is presented.

