Influence of halogen substitution on aggregation-induced near infrared fluorescence of borondifluoride complexes of 2’-hydroxychalcones

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S1. Materials and methods.

**Materials.** All solvents for synthesis were of analytic grade. Spectroscopy measurements were carried out with spectroscopic grade solvents. NMR spectra (\(^1\text{H},\ ^{19}\text{F}\)) were recorded at room temperature on a Bruker Advance 300 operating at 300 MHz and 282 MHz for \(^1\text{H}\) and \(^{19}\text{F}\), respectively. Data are listed in parts per million (ppm) and are reported relative to tetramethylsilane (\(^1\text{H}\)); residual solvent peaks of the deuterated solvents were used as an internal standard. Mass spectra and elemental analyses were realized in Spectropole de Marseille (http://www.spectropole.fr/). Solid state spectra and luminescence quantum yields were measured using an integrating sphere.

**UV-Vis-absorption spectra** were measured on a Varian Cary 50. Solid-state spectra were measured by dropcasting a solution of the compound in dry CH\(_2\text{Cl}_2\) onto a quartz plate and correcting for a scattered-light background.

**Fluorescence emission spectra** were measured on a Horiba-JobinYvon Fluorolog-3 spectrofluorimeter that was equipped with three-slit double-grating excitation and a spectrograph emission monochromator with dispersions of 2.1 nm mm\(^{-1}\) (1200 grooves mm\(^{-1}\)). Steady-state luminescence was excited by using unpolarized light from a 450-W xenon CW lamp and detected at an angle of 90° for dilute-solution measurements (10 mm quartz cell) with a red-sensitive Hamamatsu R928 photomultiplier tube for spectra up to 700 nm and a Hamamatsu R406 photomultiplier tube for spectra above 700 nm. Special care was taken to correct NIR-emission spectra that were obtained with the latter device. The detector was corrected according to the procedure described by Parker.\(^1\) The observed photomultiplier output \(A_I\) was recorded at wavelength \(\lambda\), which corresponds to the apparent emission spectrum. \(A_I\) is given by eq. (1), where \(F_I\) and \(S_I\) are the corrected emission spectrum and the spectroscopic sensitivity factor of the monochromator-photomultiplier setup, respectively.

\[
A_I = \frac{(F_I)(S_I)}{\lambda^2} \tag{1}
\]

To calculate \(S_I\), we used 4-N,N-dimethylamino-4’-nitrostilbene (DMANS) as a standard NIR fluorophore for which its corrected emission spectrum has been precisely determined.\(^2\) Luminescence quantum yields (\(\phi_I\)) were measured in dilute solutions in CH\(_2\text{Cl}_2\) with an absorbance of below 0.1 by using eq. (2), where \(A(\lambda)\) is the absorbance at the excitation wavelength (\(\lambda\)), \(n\) the refractive index, and \(I\) the integrated luminescence intensity.

\[
\frac{\phi_k}{\phi_r} = \frac{[A_k(\lambda)/A_r(\lambda)][I_k/I_r]} \tag{2}
\]

where \(A(\lambda)\) is the absorbance at the excitation wavelength (\(\lambda\)) and \(I\) the integrated luminescence intensity. Subscripts “r” and “x” stand for reference and sample, respectively. The luminescence quantum yields were not corrected by the refractive indexes. We used trisbipyridineruthenium(II) bischloride in water (\(\phi_r = 0.021\)) as reference.

**Quantum chemicals computations** were performed on isolated molecules using methods based on Density Functional Theory (DFT). Molecular structures were optimized using the code NWCHEM,\(^3\) with the PBE0 functional\(^4\) and the basis set 6-311g**. Starting from the optimized structures, using the same basis set and exchange correlation functional, the ground state dipoles have been obtained. The HOMO and LUMO orbitals have been calculated with the Quantum Espresso code\(^5\) and a PBE functional.\(^6\) The figures have been prepared with the VESTA program.\(^7\)
**X-Ray diffraction.** Powder-diffraction measurements were realized in the transmission mode by using an INEL diffractometer which was equipped with a linear detector INEL CPS 120 and a quartz curved monochromator. The radiation length was 1.54056 Å (CuKα1). The powder was deposited into glass capillaries with diameters of 0.5, 0.7, and 1 mm. For the samples in which the crystallites agglomerated into quite large pieces, the powder was broken into small parts with a sharp spatula; milling was not used so as to prevent any possible changes in the crystalline structure. Iodine-containing samples were deposited into capillaries with a diameter of 0.5 mm and those that contained chlorinewere deposited into capillaries with a diameter of 0.7 mm to diminish the X-ray absorption into the samples. The intensity data for single-crystal X-ray-diffraction were collected at RT on a Bruker-Nonius KappaCCD diffractometer by using MoKα radiation (λ=0.71073 Å). Data collection was performed with COLLECT, cell-refinement and data-reduction were performed with DENZO/SCALEPACK. The structure was solved with SIR92 and SHELXL-97 was used for full-matrix least-squares refinement. Then, the H atoms were introduced at idealized positions and constrained to their parent atom during the last refinements. Graphics were generated with MERCURY 3.10.

**S2. Syntheses**

**General synthesis of 2'-hydroxychalcone.** In a 100 mL round bottom flask, the appropriate 2'-hydroxyphenone (1 mol eq.) and the 4-methoxybenzaldehyde (1 mol eq.) were solubilized in ethanol (25mL). Sodium hydroxide (2.5 mol Eq) in 1-2 mL of water was then added to the solution. The mixture was stirred for 16 hours at 60 °C. After cooling to room temperature, the solution was acidified to pH = 1 and the precipitate was filtered off on a glass filter. The solid was recrystallized twice in a mixture of dichloromethane and ethanol to yield the pure ligand.

**General synthesis of BF₂ complexes.** To a solution of 2'-hydroxychalcone (1 mol eq) in dichloromethane in a 50 mL round bottom flask, was added boron trifluoride etherate (1.2 mol eq). This solution was stirred at reflux for 2 hours. The solution was concentrated, cooled to room temperature and the precipitate was filtered off, washed with diethyl ether and air dried yielding the pure product.

![BF₂ complex structure](image)

**Cl-Cl:** ¹H NMR(250 MHz, CDCl₃): δ 8.63 (d, 3J = 14.5 Hz, 1H), 7.84 (m, 4H), 7.41 (d, 3J = 14.5 Hz, 1H), 7.08 (d, 3J = 8.8 Hz, 2H), 3.98 (s, 3H) ppm; ¹⁹F-NMR (235 MHz, CDCl₃): δ -142.54 (¹⁹B-F, 0.2F), -142.60 (¹⁹B-F, 0.8F) ppm. HR-MS (ESI⁺) calcd for C₁₆H₁₁BCl₂F₂O₃Na⁺ m/z = 393.0042 [M + Na]⁺; found, 393.0038 [M + Na]⁺.
$^1$H NMR spectrum of Cl-Cl in CDCl$_3$.

$^{19}$F NMR spectrum of Cl-Cl in CDCl$_3$.

HR-MS spectrum (electrospray, positive mode) of Cl-Cl.
Br-Br: ¹H NMR(250 MHz, CDCl₃): δ 8.59 (d, ³J = 14.8 Hz, 1H), 8.07 (d, ⁴J = 2.2 Hz, 1H), 8.01 (d, ⁴J = 2.2 Hz, 1H), 7.77 (d, ³J = 9.3 Hz, 2H), 7.39 (d, ³J = 15.0 Hz, 1H), 7.05 (d, ³J = 9.0 Hz, 2H), 3.95 (s, 3H) ppm; ¹⁹F-NMR (235 MHz, CDCl₃): δ -142.56 (¹⁰B-F, 0.2), -142.62 (¹¹B-F, 0.8) ppm. EI-MS: (positive mode): m/z: 482.9 [M+Na]⁺, 498.9 [M+K]⁺. Elemental analysis calcd (Found) for C₁₆H₁₁BBr₂F₂O₃: C: 41.79 (41.54), H: 2.41 (2.53). HR-MS (ESI+) calcd for C₁₆H₁₁BBr₂F₂O₃Na⁺ m/z = 482.9013 [M + Na]⁺; found, 482.9016 [M + Na]⁺.

¹H NMR spectrum of Br-Br in CDCl₃.

¹⁹F NMR spectrum of Br-Br in CDCl₃.
**I-I:** $^1$H NMR (250 MHz, CDCl$_3$): $\delta$ 8.57 (d, $^3J = 15.3$ Hz, 1H), 8.42 (d, $^4J = 2.0$ Hz, 1H), 8.17 (d, $^3J = 2.0$ Hz, 1H), 7.83 (d, $^3J = 9.0$ Hz, 2H), 7.38 (d, $^3J = 15.3$ Hz, 1H), 7.05 (d, $^3J = 8.8$ Hz, 2H), 3.95 (s, 3H) ppm; $^{19}$F-NMR (235 MHz, CDCl$_3$): $\delta$ -142.51 ($^{10}$B-F, 0.2F), -142.57 ($^{11}$B-F, 0.8F) ppm. HR-MS (ESI$^+$) calcd for C$_{16}$H$_{11}$B$_2$F$_2$O$_3$Na$^+$ $m/z = 576.8754$ [M + Na]$^+$; found, 576.8752 [M + Na]$^+$.

$^1$H NMR spectrum of I-I in CDCl$_3$.

$^{19}$F NMR spectrum of I-I in CDCl$_3$.
**F-F** (this compound decomposes rapidly in CDCl$_3$ to give the free ligand): $^1$H NMR (250 MHz, CDCl$_3$): $\delta$ 8.63 (d, $^3J = 15.3$ Hz, 1H), 8.01 (s, 1H), 7.96 (1H), 7.84 (d, $^3J = 8.8$ Hz, 2H), 7.39 (d, $^3J = 15.3$ Hz, 1H), 7.07 (d, $^3J = 9.0$ Hz, 2H), 3.98 (s, 3H) ppm; $^{19}$F-NMR(235 MHz, CDCl$_3$): $\delta$ -142.77 ($^{10}$B-F, 0.4F), -142.83 ($^{11}$B-F, 1.6F) ppm. HR-MS (ESI$^+$) calcd for C$_{16}$H$_{11}$BF$_4$O$_3$Na$^+$ $m/z = 361.0633$ [M + Na]$^+$; found, 361.0630 [M + Na]$^+$.
\( ^{19} \text{F NMR of F-F in CDCl}_3 \). 

HR-MS spectrum (electrospray, positive mode) of F-F.

\[ \text{Cl-Br: } ^1 \text{H NMR (250 MHz, CDCl}_3\text{): } \delta 8.60 \text{ (d, } ^3 \text{J} = 15.2 \text{ Hz, 1H), 7.96 \text{ (d, } ^4 \text{J} = 2.3 \text{ Hz, 1H), 7.90 \text{ (d, } ^4 \text{J} = 2.5 \text{ Hz, 1H), 7.83 \text{ (d, } ^3 \text{J} = 8.3 \text{ Hz, 2H), 7.39 \text{ (d, } ^3 \text{J} = 15.0 \text{ Hz, 1H), 7.05 \text{ (d, } ^3 \text{J} = 8.3 \text{ Hz, 2H), 3.95 \text{ (s, 3H) ppm; } ^{19} \text{F-NMR (235 MHz, CDCl}_3\text{): } \delta -142.51 \text{ (}^{10} \text{B-F, 0.2F), -142.58 \text{ (}^{11} \text{B-F, 0.8F) ppm. HR-MS (ESI\textsuperscript{+}) calcd for C}_{16} \text{H}_{11} \text{BClBrF}_2 \text{O}_3 \text{Na}^+ \text{ m/z = 438.9515 [M + Na]}^+; found, 438.9515 \text{ [M + Na]}^+.} \]
1H NMR spectrum of Cl-Br in CDCl₃.

19F NMR spectrum of Cl-Br in CDCl₃.

HR-MS spectrum (electrospray, positive mode) of Cl-Br.
**Br-Cl**: $^1$H NMR (250 MHz, CDCl$_3$): $\delta$ 8.60 (d, $^3J = 14.8$ Hz, 1H), 7.96 (d, $^4J = 2.5$ Hz, 1H), 7.86 (d, $^4J = 2.5$ Hz, 1H), 7.83 (d, $^3J = 8.8$ Hz, 2H), 7.40 (d, $^3J = 14.8$ Hz, 1H), 7.05 (d, $^3J = 8.8$ Hz, 2H), 3.95 (s, 3H) ppm; $^{19}$F-NMR (235 MHz, CDCl$_3$): $\delta$ -142.59 ($^{10}$B-F, 0.2F), -142.65 ($^{11}$B-F, 0.8F) ppm. HR-MS (ESI$^+$) calcd for C$_{16}$H$_{11}$BClBrF$_2$O$_3$Na$^+$ $m/z = 438.9515$ [M + Na]$^+$; found, 438.9513 [M + Na]$^+$.

$^1$H NMR spectrum of **Br-Cl** in CDCl$_3$.

$^{19}$F NMR spectrum of **Br-Cl** in CDCl$_3$. 
HR-MS spectrum (electrospray, positive mode) of Br-Cl.

I-Cl: $^1$H NMR (250 MHz, CDCl$_3$): $\delta$ 8.58 (d, $^3J$ = 15.0 Hz, 1H), 8.17 (d, $^4J$ = 2.3 Hz, 1H), 7.89 (d, $^4J$ = 2.5 Hz, 1H), 7.82 (d, $^3J$ = 9.0 Hz, 2H), 7.39 (d, $^3J$ = 15.0 Hz, 1H), 7.05 (d, $^3J$ = 8.8 Hz, 2H), 3.95 (s, 3H) ppm; $^{19}$F-NMR (235 MHz, CDCl$_3$): $\delta$ -142.57 ($^{10}$B-F, 0.2F), -142.63 ($^{11}$B-F, 0.8F) ppm. HR-MS (ESI$^+$) calcd for C$_{16}$H$_{11}$BClF$_2$O$_3$Na$^+$ $m/z$ = 484.9398 [M + Na]$^+$; found, 484.9398 [M + Na]$^+$.

$^1$H NMR spectrum of I-Cl in CDCl$_3$. 
**19F NMR spectrum of I-Cl in CDCl₃.**

HR-MS spectrum (electrospray, positive mode) of I-Cl.

**I-Br:** ¹H NMR (250 MHz, CDCl₃): δ 8.58 (d, 3J = 14.8 Hz, 1H), 8.28 (d, 4J = 2.3 Hz, 1H), 8.02 (d, 4J = 2.5 Hz, 1H), 7.82 (d, 3J = 8.7 Hz, 2H), 7.39 (d, 3J = 14.8 Hz, 1H), 7.05 (d, 3J = 8.5 Hz, 1H), 3.95 (s, 3H) ppm; ¹³F-NMR (235 MHz, CDCl₃): δ -142.54 (¹¹B-F, 0.2F), -142.60 (¹³B-F, 0.8F) ppm. HR-MS (ESI⁺) calcd for C₁₆H₁₁BBF₂O₃Na⁺ m/z = 528.8893 [M + Na]⁺; found, 528.8893 [M + Na]⁺.
$^1$H NMR spectrum of I-Br in CDCl$_3$.

$^{19}$F NMR spectrum of I-Br in CDCl$_3$.

HR-MS spectrum (electrospray, positive mode) of I-Br.
I-F: \(^1\)H NMR (250 MHz, CDCl\(_3\)): \(\delta\) 8.58 (d, \^3J = 15.0 Hz, 1H), 8.02 (dd, \(^4J_{H-F} = 7.5\)Hz, \(^4J_{H-H} = 2.7\) Hz, 1H), 7.80 (d, \(^3J = 8.8\) Hz, 2H), 7.60 (dd, \(^4J_{H-F} = 7.5\)Hz, \(^4J_{H-H} = 2.7\) Hz, 1H), 7.36 (d, \(^3J = 14.8\) Hz, 1H), 7.04 (d, \(^3J = 8.8\) Hz, 2H), 3.95 (s, 3H) ppm; \(^19\)F-NMR (235 MHz, CDCl\(_3\)): \(\delta\) -142.81 (\(^{10}\)B-F, 0.4F), -142.87 (\(^{11}\)B-F, 1.6F) ppm. HR-MS (ESI\(^+\)) calcd for C\(_{16}\)H\(_{11}\)BIF\(_2\)O\(_3\)Na\(^+\) m/z = 468.9693 [M + Na]\(^+\); found 468.9693 [M + Na]\(^+\).

\(^1\)H NMR spectrum of I-F in CDCl\(_3\).

\(^{19}\)F NMR spectrum of I-F in CDCl\(_3\).
HR-MS spectrum (electrospray, positive mode) of I-F.
S3. Supplementary data

Table S1. Half-life ($t_{1/2}$) and kinetic rates ($k_{obs}$) for solvolysis of the 2'-hydroxychalcone borondifluoride complexes (conc. 7.5 x 10^{-6} M) in presence of 0.5% ethanol in DCM.

<table>
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<tr>
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<th>$\lambda$ / nm</th>
<th>$t_{1/2}$ / min</th>
<th>$k_{obs}$ / s^{-1}</th>
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<tr>
<td>H-H</td>
<td>455</td>
<td>240.6</td>
<td>4.8 x 10^{-5}</td>
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<tr>
<td>F-F</td>
<td>480</td>
<td>6.3</td>
<td>1.8 x 10^{-3}</td>
</tr>
<tr>
<td>Cl-Cl</td>
<td>481</td>
<td>43.3</td>
<td>2.7 x 10^{-4}</td>
</tr>
<tr>
<td>Br-Br</td>
<td>482</td>
<td>63.0</td>
<td>1.8 x 10^{-4}</td>
</tr>
<tr>
<td>I-I</td>
<td>482</td>
<td>110.0</td>
<td>1.0 x 10^{-4}</td>
</tr>
<tr>
<td>Cl-Br</td>
<td>480</td>
<td>57.8</td>
<td>2.0 x 10^{-4}</td>
</tr>
<tr>
<td>Br-Cl</td>
<td>480</td>
<td>55.9</td>
<td>2.1 x 10^{-4}</td>
</tr>
<tr>
<td>I-F</td>
<td>482</td>
<td>53.3</td>
<td>2.2 x 10^{-4}</td>
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<tr>
<td>I-Cl</td>
<td>481</td>
<td>67.4</td>
<td>1.7 x 10^{-4}</td>
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<tr>
<td>I-Br</td>
<td>483</td>
<td>83.5</td>
<td>1.4 x 10^{-4}</td>
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Table S2. Selected crystal data for compounds Cl-Cl, Br-Br, I-I, Cl-Br and Br-Cl.

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<thead>
<tr>
<th>Variable</th>
<th>Cl-Cl</th>
<th>Br-Br</th>
<th>I-I</th>
<th>Cl-Br</th>
<th>Br-Cl</th>
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<tr>
<td>Formula</td>
<td>C_{16}H_{11}BF_{2}ClO_{3}</td>
<td>C_{16}H_{11}BF_{2}BrO_{3}</td>
<td>C_{16}H_{11}BF_{2}I_{2}O_{3}</td>
<td>C_{16}H_{11}BF_{2}BrClO_{3}</td>
<td>C_{16}H_{11}BF_{2}BrClO_{3}</td>
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<tr>
<td>M / g</td>
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<td>459.88</td>
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<td>P 21/c</td>
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<td>7.6071(2)</td>
<td>8.0064(3)</td>
<td>7.5301(3)</td>
<td>7.5791(2)</td>
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<tr>
<td>b / Å</td>
<td>15.0190(4)</td>
<td>15.4687(4)</td>
<td>16.5194(5)</td>
<td>15.2840(7)</td>
<td>15.1383(4)</td>
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<tr>
<td>c / Å</td>
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<td>13.9718(3)</td>
<td>15.5770(5)</td>
<td>13.7542(5)</td>
<td>14.0950(3)</td>
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<td>123.517(2)</td>
<td>98.581(3)</td>
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<td>15111</td>
<td>16091</td>
<td>16729</td>
</tr>
<tr>
<td>Refln I &gt; 2σ(I)</td>
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<td>2528</td>
<td>2912</td>
<td>2632</td>
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</tr>
<tr>
<td>R1 I &gt; 2σ(I)</td>
<td>0.0658</td>
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<td>0.0601</td>
<td>0.0444</td>
</tr>
<tr>
<td>R1 all data</td>
<td>0.0978</td>
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<tr>
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<tr>
<td>$\Delta\rho$(+/-)/e. Å^-3</td>
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<td>0.144/-1.13</td>
<td>0.097/-1.183</td>
<td>0.069/-0.856</td>
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</tbody>
</table>
**Fig. S1** Dipole orientation calculated using DFT

**LUMO**

**HOMO**

**Cl-Br**  **Br-Cl**

**Fig. S2** HOMO and LUMO molecular orbitals for Cl-Br and Br-Cl.

**Fig. S3** Comparison of the calculated powder X-Ray diffraction patterns (▬) with the experimental ones (▬) for Cl-Cl
Fig. S4 Comparison of the calculated powder X-Ray diffraction patterns (▬) with the experimental ones (▬) for Br-Br

Fig. S5 Comparison of the calculated powder X-Ray diffraction patterns (▬) with the experimental ones (▬) for I-I
**Fig. S6** Comparison of the calculated powder X-Ray diffraction patterns (▬) with the experimental ones (▬) for Cl-Br

**Fig. S7** Comparison of the calculated powder X-Ray diffraction patterns (▬) with the experimental ones (▬) for Br-Cl
Fig. S8 Thermal ellipsoid (50%) plots of a/ Cl-Cl, b/ Br-Br and c/ I-I.
Fig. S9 Thermal ellipsoid (50%) plots of a/ Cl-Br and b/ Br-Cl.
Fig. S10 Selected views of the molecular packing for Cl-Cl: a/ and b/ along the long molecular axis (average intermolecular distance), c/ along the short molecular axis, d/ perpendicularly to the molecular plane.

Fig. S11 Selected views of the molecular packing for Br-Br: a/ and b/ along the long molecular axis (average intermolecular distance), c/ along the short molecular axis, d/ perpendicularly to the molecular plane.
**Fig. S12** Selected views of the molecular packing for I-I: a/ and b/ along the long molecular axis (average intermolecular distance), c/ along the short molecular axis, d/ perpendicularly to the molecular plane.

**Fig. S13** Selected views of the molecular packing for Cl-Br: a/ and b/ along the long molecular axis (average intermolecular distance), c/ along the short molecular axis, d/ perpendicularly to the molecular plane.
Fig. S14 Selected views of the molecular packing for Br-Cl: a/ and b/ along the long molecular axis (average intermolecular distance), c/ along the short molecular axis, d/ perpendicularly to the molecular plane.
**Fig. S15** UV/visible absorption spectra of thin films (---) and solutions in DCM (——), and fluorescence spectra of powder sample (----) and solutions in DCM (——) for a/ I-F, b/ Br-Cl, c/ Cl-Br, d/ I-Cl, e/ I-Br and f/ H-H.
S.4 References