

**Supporting Information:**

## **Structural characterization, and optical properties of two Copper(I)-Iodide BODIPY Coordination Polymers**

Hawazen Hassanain, E. Stephen Davies, William Lewis, Deborah L. Kays\* and Neil R. Champness\*

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## Experimental section

All reagents and solvents were purchased from Aldrich Chemicals, Alfa Aesar or Fisher Scientific UK, and used without further purification unless otherwise stated. Thin layer chromatography (TLC) was used to monitor ligand synthesis reactions. Column chromatography on silica gel (Merck silica gel 60, 0.2-0.5 mm, 50-130 mesh) was used for purification (unless otherwise stated).  $^1\text{H}$  and  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra were recorded at room temperature with either a Bruker AV400 or a Bruker AV3400, operating at 400 and 100 MHz, respectively.  $^{11}\text{B}$  and  $^{19}\text{F}$  NMR spectra were recorded at room temperature with Bruker AV3400, operating at 128 and 376 MHz, respectively. Chemical shifts are quoted in ppm relative to TMS ( $^1\text{H}$  and  $^{13}\text{C}\{^1\text{H}\}$ ).  $\text{BF}_3\cdot\text{OEt}_2$  was used as an external reference for  $^{11}\text{B}$  NMR measurements and  $\text{CFCl}_3$  as an external reference for  $^{19}\text{F}$  NMR measurements.

## Spectroscopic and Analytical Measurements

Absorption UV/Vis spectra of both solutions and thin films were measured with a Perkin Elmer Lambda 25 UV/Vis spectrometer. For solution spectra a 1 cm pathlength quartz cuvette was used. Excitation and emission photoluminescence spectra of solution samples were performed using an Edinburgh Instruments FLS920 Fluorometer. The fluorescence spectra were recorded in standard quartz fluorescence cuvettes,  $l = 1 \times 1$  cm. All spectroscopy experiments were performed using spectrophotometric grade solvent and solutions never exceeded  $A = 0.10$  at the excitation wavelength, or any longer wavelength, to minimise inner filter effects. Solution fluorescence spectra were recorded as aerated solutions using a Jobin Yvon Horiba FluoroMax-3 spectrometer at ambient temperature in a 1cm pathlength quartz cuvette. Quantum yields were calculated by comparison with the fluorescence observed for perylene orange ( $\Phi = 0.99$  in  $\text{CHCl}_3$ ) under identical conditions of irradiation ( $\lambda_{\text{Excitation}} 483$  nm).<sup>1</sup>

Excitation and emission photoluminescence spectra of the powder, and thin film samples were performed using an FLS980 Spectrometer. Dye films were prepared by drop casting a solution of **1** or **2** from a  $\text{CH}_2\text{Cl}_2$  solution on to a quartz substrate, the sample was then left to dry. Diffuse UV-vis reflectance spectra were measured on a UV Vis NIR Agilent Cary Spectrometer equipped with an integrating sphere accessory. Fluorescence micrograph images of single crystals were recorded using an Olympus IX73. The crystals were excited at 540-550 nm. Powder XRD measurements (Cu-K $\alpha$  radiation) were made using powdered samples placed on circular kapton polyimide thin film to record the XRD pattern.

Single crystals were selected and mounted using fomblin film on a micromount. Data was collected with an Agilent GV1000, Atlas diffractometer (**1a**), an Agilent GV1000, TitanS2 (**1b**, **2**, **3**) equipped with an area detector, or a XtaLAB PRO MM007 diffractometer equipped with a PILATUS3 R 200K Hybrid Pixel Array detector (**4**). Crystals were kept at 120(2) K during data collection and monochromated CuK $\alpha$  ( $\lambda = 1.54184$ ) radiation was used in each case. Using Olex2,<sup>2</sup> the structures were solved with the ShelXT<sup>3</sup> structure solution program using Intrinsic Phasing and refined with the ShelXL<sup>4</sup> refinement package using Least Squares minimisation.

## Synthetic Procedures.

Compound **1** was synthesised according to literature procedures.<sup>5</sup>

Crystal data for **1a**: C<sub>29</sub>H<sub>25</sub>B<sub>1</sub>N<sub>4</sub>F<sub>2</sub>, triclinic, space group *P*-1, *a* = 6.2631(5) Å, *b* = 11.5815(7) Å, *c* = 16.4310(8) Å,  $\alpha$  = 90.269(4)°,  $\beta$  = 91.458(5)°,  $\gamma$  = 105.041(6)°, *V* = 1150.56(13) Å<sup>3</sup>, *Z* = 2, *D*<sub>calc</sub> = 1.381 g cm<sup>-3</sup>,  $\mu$  = 0.757 mm<sup>-1</sup>, *F*(000) = 500, a total of 7918 reflections were collected, of which 4495 were unique, with *R*<sub>int</sub> = 0.0302. Final *R*<sub>1</sub> (*wR*<sub>2</sub>) = 0.0448 (0.1271) with GOF = 1.03.

Crystal data for **1b**: C<sub>29</sub>H<sub>25</sub>B<sub>1</sub>N<sub>4</sub>F<sub>2</sub>, monoclinic, space group *I*2/*a*, *a* = 13.5686(4) Å, *b* = 13.2178(5) Å, *c* = 13.7790(5) Å,  $\beta$  = 105.947(4)°, *V* = 2376.12(15) Å<sup>3</sup>, *Z* = 4, *D*<sub>calc</sub> = 1.337 g cm<sup>-3</sup>,  $\mu$  = 0.730 mm<sup>-1</sup>, *F*(000) = 1000, a total of 4769 reflections were collected, of which 2358 were unique, with *R*<sub>int</sub> = 0.0191. Final *R*<sub>1</sub> (*wR*<sub>2</sub>) = 0.0405 (0.1102) with GOF = 1.040.

Synthesis of **2**: A solution of 2,6-diiodo-1, 3, 5,7-dimethyl-8-phenyl-4,4 difluoroboradiazaindacene (100 mg, 0.19 mmol) in a mixture of solvents, 1,4-dioxane (60 mL) and water (6 mL), was added to (90 mg, 0.78 mmol) of pyrimidine 4-boronic acid and Cs<sub>2</sub>CO<sub>3</sub> (254 mg, 0.78mmol). The solution was bubbled with dry dinitrogen gas for 30 minutes. Tetrakis(triphenylphosphine)palladium(0) (56 mg, 0.048mmol) was added under a dinitrogen atmosphere. The reaction mixture was refluxed in the absence of light until the reaction was complete. The crude product was purified using column chromatography (ethyl acetate: methanol = 10:1) to afford **3** as a red solid, 50 mg, yield 60%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  9.21 (s, 1H); 8.68 (s, 2H); 7.72-7.49 (m, 7H), 7.27-7.39 (m, 1H), 2.60(s, 6H), 1.61 (s, 6H); 1.37 (s, 2H); 1.28 (s, 1H); <sup>13</sup>C NMR (100MHz, CDCl<sub>3</sub>) 157.57, 157.42, 132.15, 132.05, 131.96, 131.94, 129.68, 128.57, 128.45, 127.86, 127.61, 77.33, 77.02, 76.70, 13.36, 12.78; <sup>11</sup>B-NMR (128 MHz, CDCl<sub>3</sub>)  $\delta$  0.88 (t, *J* = 32.14 Hz); <sup>19</sup>F-NMR: (376 MHz, CDCl<sub>3</sub>)  $\delta$ -145.74 (q, *J* = 32.11 Hz). (HESI/MeOH): *m/z* calculated 479.1973 observed 479.1964, ([*M*-H]<sup>-</sup>, 100%). FT-IR(ATR, cm<sup>-1</sup>): 441w, 502m, 537s, 690s, 522s, 632w, 722s, 756w, 835w, 931w, 999m, 1070s, 1121s, 1284s, 1312 m, 1438m, 1486w, 1520w, 1589w, 1729m, 2850w, 2923m, 2949w, 3059w.

Crystal data for **2**: C<sub>27</sub>H<sub>23</sub>BN<sub>6</sub>F<sub>2</sub>. monoclinic, space group *P*2<sub>1</sub>/*c*, *a* = 11.2952(3) Å, *b* = 17.0907(6) Å, *c* = 12.0417(3),  $\beta$  = 94.541(3)°, *V* = 2317.27(12)Å<sup>3</sup>, *Z* = 4, *D*<sub>calc</sub> = 1.377g cm<sup>-3</sup>,  $\mu$  = 0.780 mm<sup>-1</sup>, *F*(000) = 1000. A total of 11672 reflections were collected, of which 4529 were unique, with *R*<sub>int</sub> = 0.0365. Final *R*<sub>1</sub> (*wR*<sub>2</sub>)= 0.0414 (0.1011) with GOF = 1.039.

Synthesis of **3**: **3** was synthesised by reaction of CuI (3mg, 0.1mmol) and **1** (35 mg, 0.07mmol) in 1ml of MeCN in a sealed scintillation vial. The mixture was heated in an oven at 55 °C for 3 days, which yielded brown shaped crystals, 30 mg, yield 95%. FT-IR(ATR, cm<sup>-1</sup>): 443w, 467w, 504m, 515m, 523m, 533s, 580s, 673m, 691s, 718s, 753w, 796m, 837w, 844w, 864w, 995s, 1065s, 1085s, 1120s, 1176w, 1180s, 1241m, 1290w, 1307m, 1389m, 1420m, 1440m, 1461m, 1604w, 1730m, 1528s, 2850w, 2926w, 3059w.

Crystal data for **3**: C<sub>29</sub>H<sub>25</sub>BCu<sub>2</sub>F<sub>2</sub>I<sub>2</sub>N<sub>4</sub>. Triclinic, space group *P*-1 *a* = 9.8116(11) Å, *b* = 10.9371(10) Å, *c* = 13.6945(12), α = 89.204(7)°, β = 87.705(8)°, γ = 78.296(8)°, *V* = 1437.8(2) Å<sup>3</sup>, *Z* = 2, *D*<sub>calc</sub> = 1.985 g cm<sup>-3</sup>, μ = 19.014 mm<sup>-1</sup>, *F*(000) = 828. A total of 9947 reflections were collected, of which 5588 were unique, with *R*<sub>int</sub> = 0.0791. Final *R*<sub>1</sub> (*wR*<sub>2</sub>) = 0.0758 (0.1993) with GOF = 1.049.

Synthesis of **4**: **4** was synthesised by slow solvent diffusion between an upper layer of CuI (3mg, 0.1mmol) in MeCN (0.4 ml) and a lower layer of **2** (37mg, 0.07mmol) in CHCl<sub>3</sub> (0.4ml) to yield brown crystals, 25 mg, yield 40 %. FT-IR(ATR, cm<sup>-1</sup>): 439m, 457m, 506m, 515m, 523m, 535s, 582w, 617w, 693m, 720s, 751m, 844w, 864w, 926w, 955w, 993w, 1071m, 1120m, 1182m, 1253m, 1313w, 1434m, 1471w, 1485w, 1537w, 1590w, 1730m, 2848w, 2920 w, 3055w.

Crystal data for **4**: C<sub>27</sub>H<sub>23</sub>BCu<sub>2</sub>F<sub>2</sub>I<sub>2</sub>N<sub>6</sub>. Monoclinic, space group *P*21/*c*. *a* = 14.6653(4) Å, *b* = 9.0291(3)Å, *c* = 12.2807(3), β = 93.859(2)°, *V* = 162247(8) Å<sup>3</sup>, *Z* = 2, *D*<sub>calc</sub> = 1.763 g cm<sup>-3</sup>, μ = 16.870 mm<sup>-1</sup>, *F*(000) = 828. A total of 9721 reflections were collected, of which 3267 were unique, with *R*<sub>int</sub> = 0.0446. Final *R*<sub>1</sub> (*wR*<sub>2</sub>) = 0.0612 (0.2068) with GOF = 1.086.

For **4** disorder was observed in the position of the central dipyrin and BF<sub>2</sub> core of the ligand. The disorder was modelled over two equally occupied components, appropriate enhanced rigid bond and similarity restraints were applied to the displacement parameters of these atoms. With exceptions noted below, hydrogen atoms were first located in electron difference maps: they were then placed in geometrically calculated positions and thereafter allowed to ride on their parent atoms. The methyl groups were refined as idealised rotating groups.

## Supplementary Tables

**Table S1.**

Bond and angles **1b, 2.**

|  | <b>1a</b> | <b>2</b>   |  | <b>1b</b>  |
|--|-----------|------------|--|------------|
| <b>F<sub>1</sub>-B<sub>1</sub></b>               | 1.384(4)  | 1.389(2)   | <b>F<sub>1</sub>-B<sub>1</sub></b>               | 1.384(4)   |
| <b>F<sub>2</sub>-B<sub>1</sub></b>               | 1.389(4)  | 1.386(2)   | <b>F<sub>1</sub>-B<sub>1</sub></b>               | 1.389(4)   |
| <b>N<sub>3</sub>-B<sub>1</sub></b>               | 1.549(4)  | 1.552(2)   | <b>N<sub>2</sub>-B<sub>1</sub></b>               | 1.5484(18) |
| <b>N<sub>4</sub>-B<sub>1</sub></b>               | 1.561(4)  | 1.551(2)   | <b>N<sub>2</sub>-B<sub>1</sub></b>               | 1.5484(18) |
| <b>F<sub>1</sub>-B<sub>1</sub>-F<sub>2</sub></b> | 110.40(3) | 109.71(15) | <b>F<sub>1</sub>-B<sub>1</sub>-F<sub>1</sub></b> | 109.34(17) |
| <b>N<sub>4</sub>-B<sub>1</sub>-N<sub>4</sub></b> | 106.40(2) | 106.35(14) | <b>N<sub>2</sub>-B<sub>1</sub>-N<sub>2</sub></b> | 106.93(16) |

Selected lengths (Å) (°) for **1a**,

**Table S2.** Bond lengths (Å), and angles (°) for **3.**

| <b>3</b>                                  |           |  |           |
|---|-----------|--|-----------|
| <b>I1-Cu2<sup>1</sup></b>                 | 2.698(2)  | <b>I1<sup>1</sup>-Cu2-I1<sup>3</sup></b> | 118.45(7) |
| <b>I1-Cu2<sup>2</sup></b>                 | 2.661(2)  | <b>I1<sup>1</sup>-Cu2-I2<sup>3</sup></b> | 108.72(7) |
| <b>I1-Cu1</b>                             | 2.614(2)  | <b>I1<sup>3</sup>-Cu2-I2<sup>3</sup></b> | 105.76(7) |
| <b>I2-Cu2<sup>1</sup></b>                 | 2.716(2)  | <b>N4-Cu2-I1<sup>3</sup></b>             | 109.70(3) |
| <b>I2-Cu1</b>                             | 2.502(2)  | <b>N4-Cu2-I1<sup>1</sup></b>             | 108.70(3) |
| <b>Cu2-N4</b>                             | 2.029(10) | <b>N4-Cu2-I2<sup>3</sup></b>             | 104.60(3) |
| <b>Cu1-N1</b>                             | 1.974(9)  | <b>I2-Cu1-I1</b>                         | 115.10(7) |
| <b>Cu2<sup>1</sup>-I1-Cu2<sup>2</sup></b> | 61.55(7)  | <b>I2-Cu1-Cu2<sup>2</sup></b>            | 65.30(7)  |
| <b>Cu1-I1-Cu2<sup>2</sup></b>             | 56.94(6)  | <b>N1-Cu1-I1</b>                         | 116.30(3) |
| <b>Cu1-I1Cu2<sup>1</sup></b>              | 72.97(7)  | <b>N1-Cu1-I2</b>                         | 125.10(3) |
| <b>Cu1-I2-Cu2<sup>2</sup></b>             | 57.91(6)  | <b>C25-N4-Cu2</b>                        | 122.40(8) |
| <b>C26-N4-Cu2</b>                         | 119.30(8) |  |           |

**Table S3.** Bond lengths (Å) and angles (°) for **4.**

| <b>4</b>                  |            |                               |            |
|---------------------------|------------|-------------------------------|------------|
| <b>I1-Cu2<sup>1</sup></b> | 2.6132(11) | <b>N27-Cu2-I1</b>             | 108.85(18) |
| <b>I1-Cu2<sup>2</sup></b> | 2.6512(12) | <b>N27-Cu2-I1<sup>1</sup></b> | 101.70(2)  |

|   |           |   |            |
|---|-----------|---|------------|
| <b>Cu2-N27</b>                            | 2.059(7)  | <b>N27-Cu2-Cu2<sup>1</sup></b>            | 122.77(19) |
| <b>Cu1-N29<sup>2</sup></b>                | 2.057(6)  | <b>N29<sup>2</sup>-Cu2-I<sup>1</sup></b>  | 108.45(19) |
| <b>N29<sup>2</sup>-Cu2Cu2<sup>1</sup></b> | 125.20(2) | <b>N29<sup>2</sup>-Cu2-I1<sup>1</sup></b> | 104.13(18) |
| <b>I1-Cu2<sup>1</sup>-I1<sup>1</sup></b>  | 60.20(4)  | <b>C26-N27-Cu2</b>                        | 123.70(5)  |
| <b>Cu2-I<sup>1</sup>-Cu2<sup>1</sup></b>  | 58.11(4)  | <b>C28-N27-Cu2</b>                        | 119.00(5)  |
| <b>Cu2<sup>1</sup>Cu2I<sup>1</sup></b>    | 61.69(4)  | <b>C28-N29-Cu2<sup>3</sup></b>            | 119.30(5)  |

## Supplementary Figures

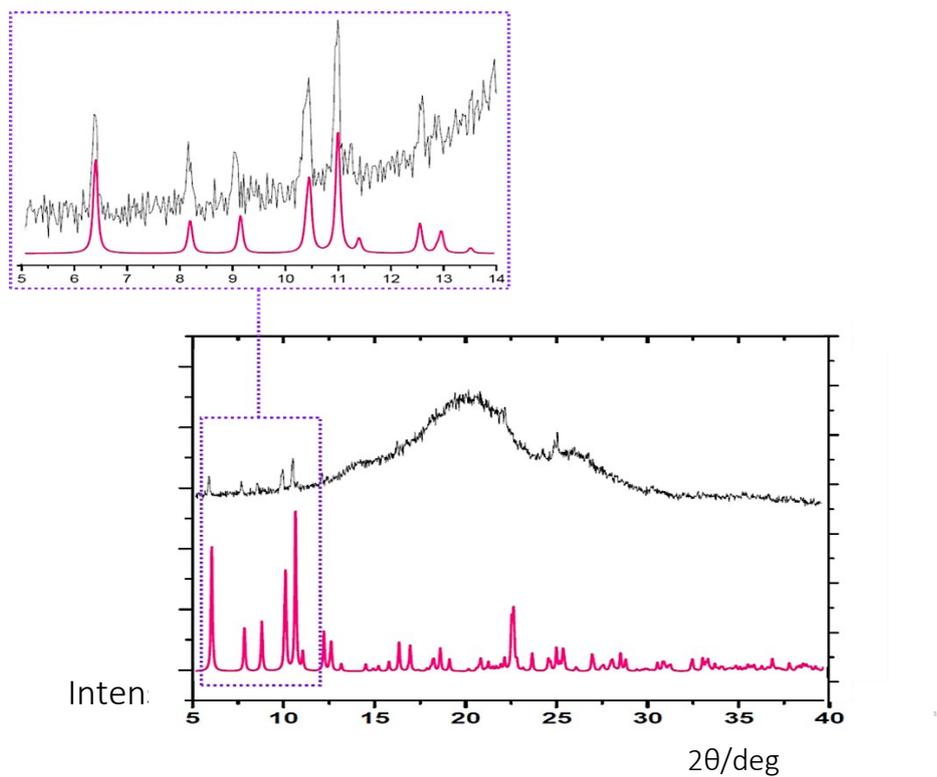


Figure S1. Calculated PXRD pattern for **3** (pink) and experimental pattern (Black).

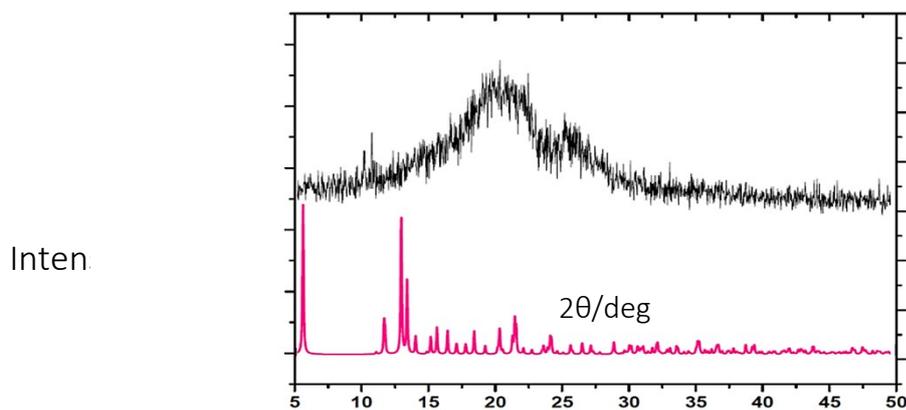


Figure S2. Calculated PXRD pattern for **4** (pink) and experimental pattern (Black). Pattern indicates losing of crystallinity upon drying and grinding.



Figure S3. Photographs showing the differences in colour of **1** and **2** as crystals, solid powder, thin film and solution in  $\text{CH}_2\text{Cl}_2$  (left to right, respectively).

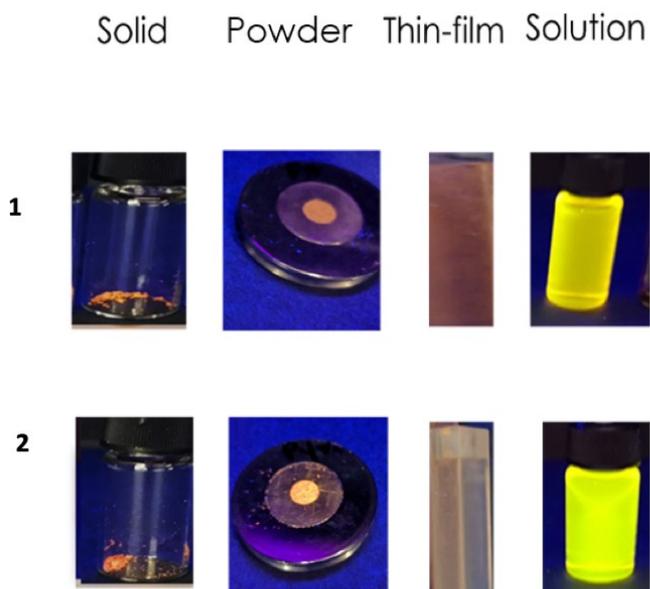


Figure S4. Photographs showing the differences in the colour of fluorescence for **1** and **2** as a solid, powder, thin film and solution in  $\text{CH}_2\text{Cl}_2$  (left to right, respectively).

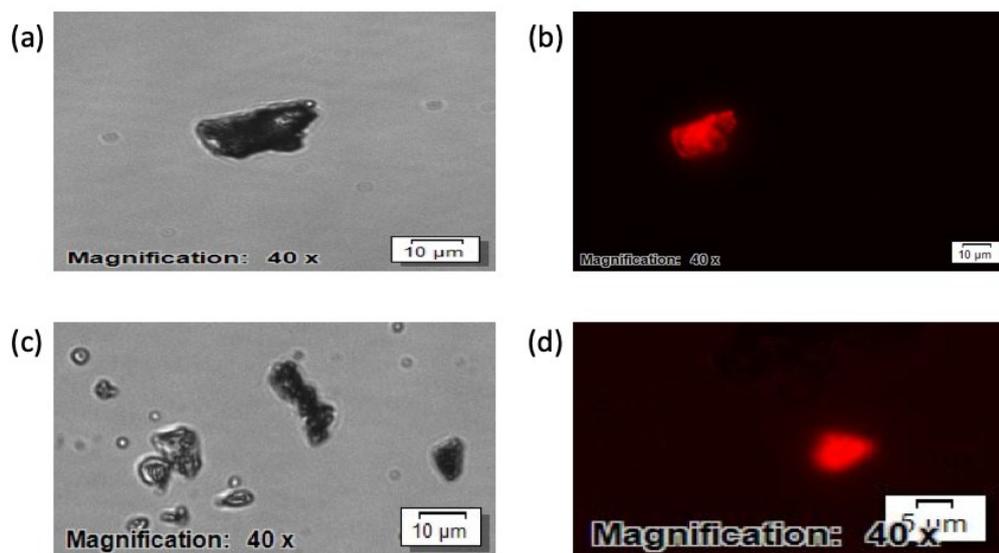


Figure S5. Micrograph images of single crystals of (a) **1**, (c) **2** and corresponding fluorescence micrograph images of single crystals of (b) **1**, (d) **2**.

## References

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