

## Supplementary Information

### Aggregation-Induced Emission Enhancement in Boron Difluoride Complexes of 3-Cyanoformazanates

Ryan R. Maar and Joe B. Gilroy\*

Department of Chemistry and the Centre for Advanced Materials and Biomaterials  
Research (CAMBR), The University of Western Ontario, London, Ontario, N6A 5B7  
(Canada). Tel. +1-519-661-2111 ext. 81561. Email: joe.gilroy@uwo.ca

#### Table of Contents

Experimental section.....	S2
Spectroscopic and electrochemical data of BF <sub>2</sub> 3-cyanoformazanates <b>5a-c</b> .....	S5
<sup>1</sup> H and <sup>13</sup> C NMR spectra.....	S6
UV-vis emission spectra of BF <sub>2</sub> 3-cyanoformazanates <b>5a-c</b> .....	S8
Detector correction provided by Photon Technology International .....	S9
Cyclic voltammograms of BF <sub>2</sub> 3-cyanoformazanates <b>5a-c</b> .....	S9
X-ray crystallographic data of BF <sub>2</sub> 3-cyanoformazanates <b>5a-c</b> .....	S10
UV-vis absorbance and emission spectra of thin-films of <b>5b</b> and <b>5c</b> .....	S15
References.....	S16

## Experimental

### General Considerations

Reagents were purchased from Sigma-Aldrich, Alfa Aesar, or Matrix Scientific and used as received unless otherwise specified. Solvents were purchased from Caledon Laboratories, dried using an Innovative Technologies Inc. solvent purification system, collected under vacuum, and stored under nitrogen atmosphere containing 4 Å molecular sieves. The synthesis, characterization, and X-ray crystallographic data of 1,5-bis(4-methoxyphenyl)-3-cyanoformazan, 1,5-bis(2-methoxyphenyl)-3-cyanoformazan, **5a**, and **5b** have previously been reported.<sup>1,2</sup> NMR spectra were recorded on 400 MHz (<sup>1</sup>H: 399.8 MHz, <sup>11</sup>B: 128.3 MHz, <sup>19</sup>F: 376.1 MHz) or 600 MHz (<sup>1</sup>H: 599.5 MHz, <sup>13</sup>C: 150.8 MHz) Varian INOVA spectrometers. <sup>1</sup>H NMR spectra were referenced to residual CHCl<sub>3</sub> (δ = 7.27 ppm) and <sup>13</sup>C NMR spectra were referenced to CDCl<sub>3</sub> (δ = 77.0 ppm). <sup>11</sup>B spectra were referenced to BF<sub>3</sub>·OEt<sub>2</sub> at δ = 0 ppm, and <sup>19</sup>F spectra were referenced to CFCl<sub>3</sub> at δ = 0 ppm. Mass spectrometry data were recorded in positive-ion mode using a high-resolution Finnigan MAT 8200 spectrometer using electron impact ionization. Thin-film samples of **5b** and **5c** were prepared by spin coating the appropriate sample onto a glass substrate from a 20 mg mL<sup>-1</sup> solution of chlorobenzene. Samples were loaded onto the substrate using a 1 mL syringe and allowed to stand for 1 min before being spun at a rate of 3000 rpm for 30 seconds. Solution and thin-film UV-vis absorption spectra were recorded using a Cary 5000 UV-Vis-NIR spectrophotometer. For solution data, molar extinction coefficients were determined from the slope of a plot of absorbance against concentration using four solutions with known concentrations ranging between 10 and 100 μM. Infrared spectra were recorded on a KBr disk using a Bruker Vector 33 FT-IR spectrometer. Emission spectra were obtained using a Photon Technology International QM-4 SE spectrofluorometer. Excitation wavelengths were chosen based on absorption maxima from the respective UV-vis absorption spectrum in THF. Fluorescence quantum yields were calculated relative to ruthenium tris(bipyridine) hexafluorophosphate by methods described by Fery-Forgues and coworkers.<sup>3</sup>

## Electrochemical Methods

Cyclic voltammetry experiments were performed with a Bioanalytical Systems Inc. (BASi) Epsilon potentiostat and analyzed using BASi Epsilon software. Typical electrochemical cells consisted of a three-electrode setup including a silver *pseudo* reference electrode, glassy carbon working electrode, and platinum counter electrode. Experiments were run at a scan rate of 100 mV s<sup>-1</sup> in degassed acetonitrile solutions of the analyte (~1 mM) and electrolyte (0.1 M *n*Bu<sub>4</sub>NPF<sub>6</sub>). Cyclic voltammograms were referenced relative to the ferrocene/ferrocenium redox couple (~1 mM internal standard) and corrected for internal cell resistance using the BASi Epsilon software.

## X-ray Crystallography Methods

Single crystals for X-ray diffraction studies of **5c** were grown by slow diffusion of hexanes into a saturated solution of the compound in dichloromethane. The samples were mounted on a Mitegen polyimide micromount with a small amount of Paratone N oil. X-ray measurements for **5c** were made on a Nonius KappaCCD Apex2 at a temperature of 110 K. The data collection strategy was a number of  $\omega$  and  $\phi$  which collected data over a range of angles,  $2\theta$ . The frame integration was performed using SAINT.<sup>4</sup> The resulting raw data was scaled and absorption corrected using a multi-scan averaging of symmetry equivalent data using SADABS.<sup>5</sup> The structure was solved by using a dual space methodology using the SHELXT program.<sup>6</sup> All non-hydrogen atoms were obtained from the initial solution. The hydrogen atoms were introduced at idealized positions and were allowed to refine isotropically. The structural model was fit to the data using full matrix least-squares based on  $F^2$ . The calculated structure factors included corrections for anomalous dispersion from the usual tabulation. The structure was refined using the SHELXL-2014 program from the SHELXTL program package.<sup>7</sup>

CCDC-1455864 and Tables S2 and S3 contain the supporting crystallographic data for this paper. This data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

### Preparation of 1,5-bis(2,6-dimethoxyphenyl)-3-cyanoformazan

In air, cyanoacetic acid (0.51 g, 6.0 mmol) and sodium hydroxide (3.27 g, 81.8 mmol) were dissolved in deionized water (55 mL). The colourless solution was cooled to 0 °C and stirred for 1 h. In a separate flask, 2,6-dimethoxyaniline (1.80 g, 11.8 mmol) was combined with concentrated hydrochloric acid (3.50 mL, 42.0 mmol) in deionized water (20 mL) and stirred for 30 min at 0 °C. A solution of sodium nitrite (0.92 g, 13 mmol) in deionized water (3 mL) was cooled to 0 °C in an ice bath for 15 min before being added dropwise over a 30 min period to the 2,6-dimethoxyaniline solution. The resulting red/yellow diazonium salt solution was stirred for 45 min at 0 °C before it was added to the alkaline cyanoacetic acid solution described above over a 20 min period. Upon addition, the solution turned blood red and a precipitate of the same colour formed. The mixture was stirred for 3 h before the precipitate was collected by vacuum filtration to afford a red solid. The filtrate was neutralized with 1 M HCl, extracted into dichloromethane (3 × 100 mL), washed with deionized water (3 × 100 mL) and brine (1 × 150 mL), dried over MgSO<sub>4</sub>, gravity filtered, and concentrated *in vacuo* to afford a second portion of 1,5-bis(2,6-dimethoxyphenyl)-3-cyanoformazan as a red solid. Both solids were combined and purified by flash column chromatography (dichloromethane, neutral alumina) and then recrystallized from methanol to afford 1,5-bis(2,6-dimethoxyphenyl)-3-cyanoformazan as a dark-red microcrystalline solid. Yield = 2.02 g, 92%; Mp: 133–135 °C. <sup>1</sup>H NMR (599.5 MHz, CDCl<sub>3</sub>): δ 12.60 (s, 1H, NH), 7.22 (t, <sup>3</sup>J<sub>HH</sub> = 8 Hz, 2H, aryl CH), 6.66 (d, <sup>3</sup>J<sub>HH</sub> = 8 Hz, 4H, aryl CH), 3.89 (s, 12H, OCH<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (150.8 MHz, CDCl<sub>3</sub>): δ 153.5, 129.5, 126.8, 125.6, 114.9, 105.0, 56.4. FT-IR (KBr): 3063 (m), 3011 (m), 2960 (m), 2838 (m), 2221 (s), 1589 (s), 1522 (s), 1481 (s), 1456 (m), 1260 (s), 1112 (s), 1026 (s) cm<sup>-1</sup>. UV-vis (THF): λ<sub>max</sub> 442 nm (ε = 9,200 M<sup>-1</sup> cm<sup>-1</sup>); 362 nm (18,675 M<sup>-1</sup> cm<sup>-1</sup>). MS (EI = +ve mode): exact mass calculated for [C<sub>18</sub>H<sub>19</sub>N<sub>5</sub>O<sub>4</sub>]<sup>+</sup>: 369.1437; exact mass found: 369.1431; difference: -1.6 ppm.

### Preparation of BF<sub>2</sub> Formazanate Complex 5c (Ar<sub>1</sub> = Ar<sub>5</sub> = 2,6-dimethoxyphenyl):

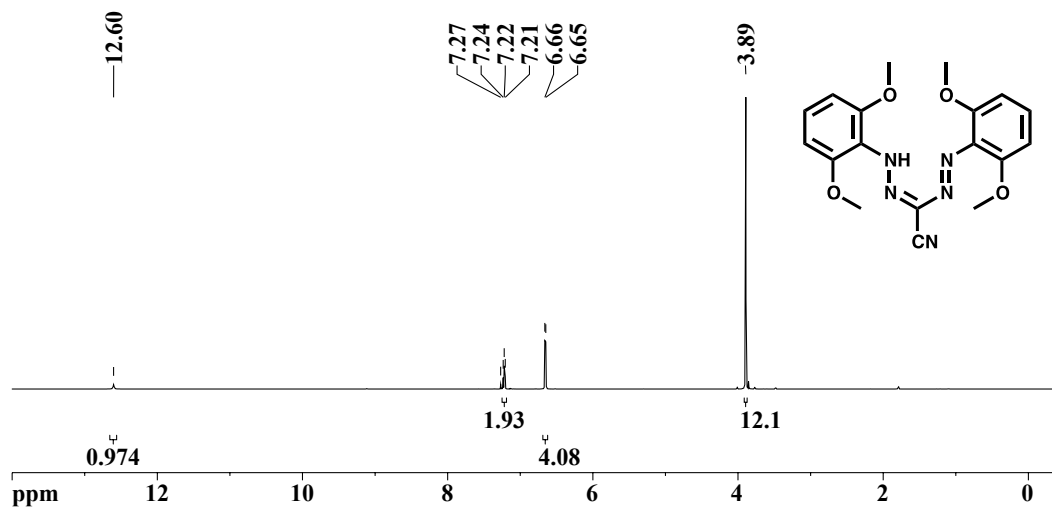
Under N<sub>2</sub>, 1,5-bis(2,6-dimethoxyphenyl)-3-cyanoformazan (1.04 g, 2.86 mmol) was dissolved in dry toluene (100 mL) before anhydrous triethylamine (2.61 g, 3.60 mL,

25.8 mmol) was added and the solution was stirred for 30 min. Boron trifluoride diethyl etherate (6.09 g, 5.30 mL, 42.9 mmol) was then added and the solution was heated to 80 °C for 18 h. The colour of the solution gradually changed from dark red to orange/yellow. At this time, the solution was cooled to 20 °C and deionized water (25 mL) was added to quench any reactive boron-containing species. The mixture was washed with deionized water (3 × 50 mL), dried over MgSO<sub>4</sub>, gravity filtered, and concentrated *in vacuo* to afford **5c** as an orange solid. The crude solid was purified via flash column chromatography (dichloromethane, neutral alumina) and triturated with ice-cold methanol to afford **5c** as bright orange microcrystalline solid. Yield = 1.15 g, 96%; Mp: 184–186 °C. <sup>1</sup>H NMR (599.5 MHz, CDCl<sub>3</sub>): δ 7.33 (t, <sup>3</sup>J<sub>HH</sub> = 8 Hz, 2H, aryl CH), 6.61 (d, <sup>3</sup>J<sub>HH</sub> = 8 Hz, 4H, aryl CH), 3.82 (s, 12H, OCH<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (150.8 MHz, CDCl<sub>3</sub>): δ 156.1, 131.8, 121.4, 114.0, 104.5, 56.4. <sup>11</sup>B NMR (128.3 MHz, CDCl<sub>3</sub>): δ -2.6 (t, <sup>1</sup>J<sub>BF</sub> = 16 Hz). <sup>19</sup>F (376.1 MHz, CDCl<sub>3</sub>): δ -162.2 (q, <sup>1</sup>J<sub>FB</sub> = 16 Hz). FT-IR (KBr): 3075 (m), 2956 (s), 2942 (s), 2830 (m), 2219 (m), 1432 (s), 1330 (s), 1245 (s), 1026 (s), 943 (s) cm<sup>-1</sup>. UV-vis (THF): λ<sub>max</sub> 434 nm (ε = 13,900 M<sup>-1</sup> cm<sup>-1</sup>). MS (EI = +ve mode): exact mass calculated for [C<sub>18</sub>H<sub>18</sub>BF<sub>2</sub>N<sub>5</sub>O<sub>4</sub>]<sup>+</sup>: 417.1420; exact mass found: 417.1421; difference: +0.2 ppm.

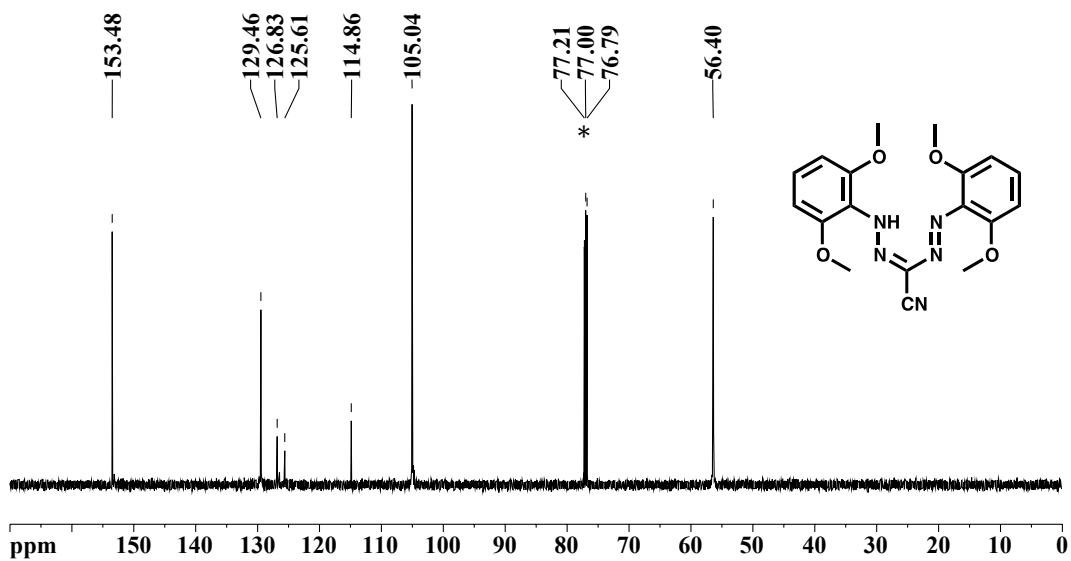
**Table S1** Spectroscopic and electrochemical data for BF<sub>2</sub> formazanates **5a–c**.

	In solution						Thin film	
	λ <sub>abs</sub> (nm) ε (M <sup>-1</sup> cm <sup>-1</sup> ) <sup>a</sup>	λ <sub>em</sub> (nm) Φ <sub>F</sub> , THF <sup>a,b</sup>	λ <sub>abs</sub> (nm) Aggr <sup>c</sup>	λ <sub>em</sub> (nm) Aggr <sup>c</sup>	E <sup>o</sup> <sub>red1</sub> <sup>d</sup> (V)	E <sup>o</sup> <sub>red2</sub> <sup>d</sup> (V)	λ <sub>abs</sub> (nm)	λ <sub>em</sub> (nm)
<b>5a</b> <sup>1</sup>	556, 33,400	662, 0.46	592	702	-0.68	-1.82	–	–
<b>5b</b> <sup>2</sup>	456, 10,100	590, 0.03	517	610	-0.75	-1.92	476	616
<b>5c</b>	434, 13,900	556, <0.01	493	580	-0.90	-2.09	443	584

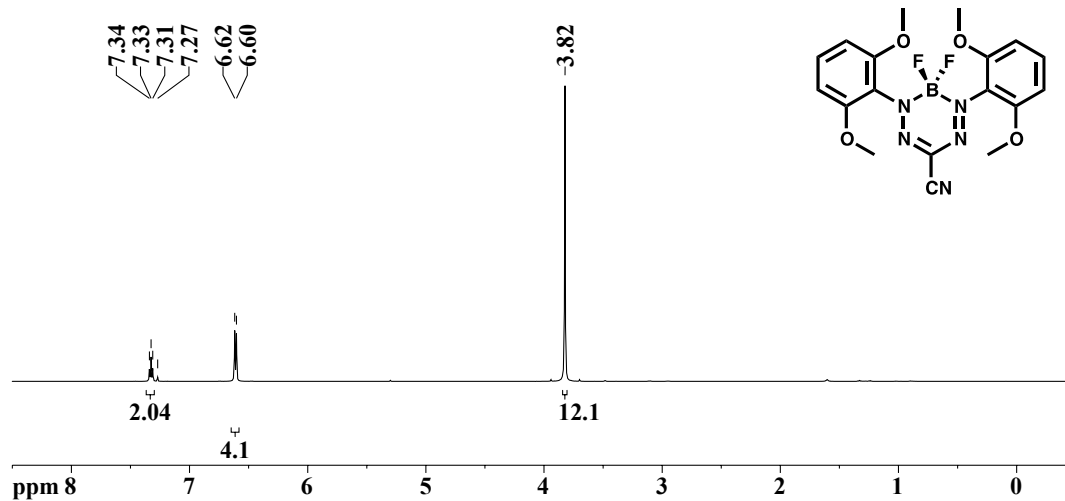
<sup>a</sup>Spectra were recorded for 10 μM solutions in dry, degassed THF. <sup>b</sup>Quantum yield experiments were measured using ruthenium tris(bipyridine) hexafluorophosphate as a relative standard<sup>3,8</sup> and corrected for detector non-linearity (Fig. S6). <sup>c</sup>Spectra were recorded at a concentration of 250 μM in a THF-water mixture with water volume fraction of 95% at 25 °C. <sup>d</sup>Cyclic voltammetry experiments were conducted in dry, degassed acetonitrile containing ~1 mM analyte and 0.1 M *n*Bu<sub>4</sub>NPF<sub>6</sub> at a scan rate of 100 mV s<sup>-1</sup>. All voltammograms were internally referenced to the ferrocene/ferrocenium redox couple.



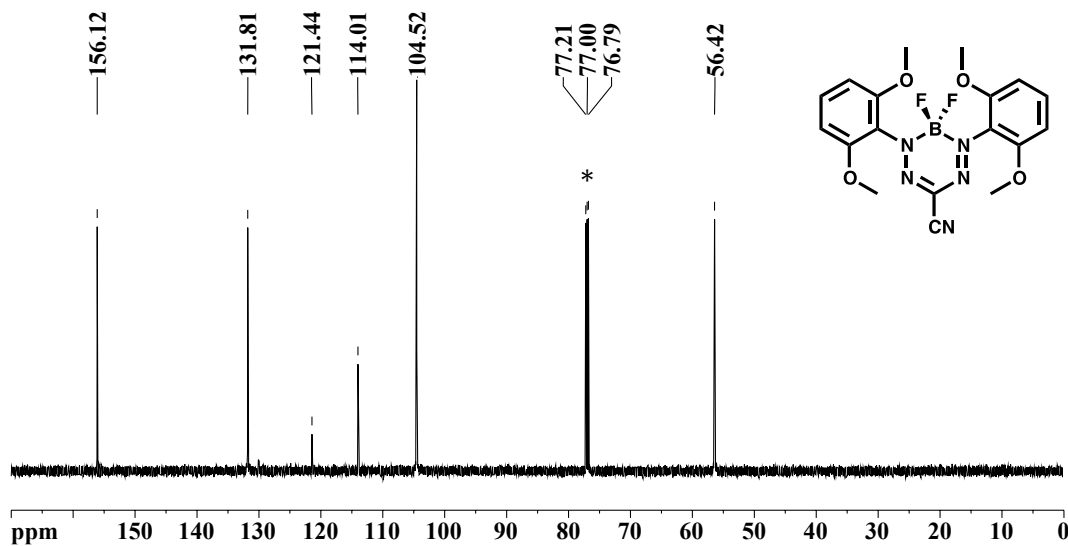
**Fig. S1**  $^1\text{H}$  NMR spectrum of 1,5-bis(2,6-dimethoxyphenyl)-3-cyanoformazan in  $\text{CDCl}_3$ .



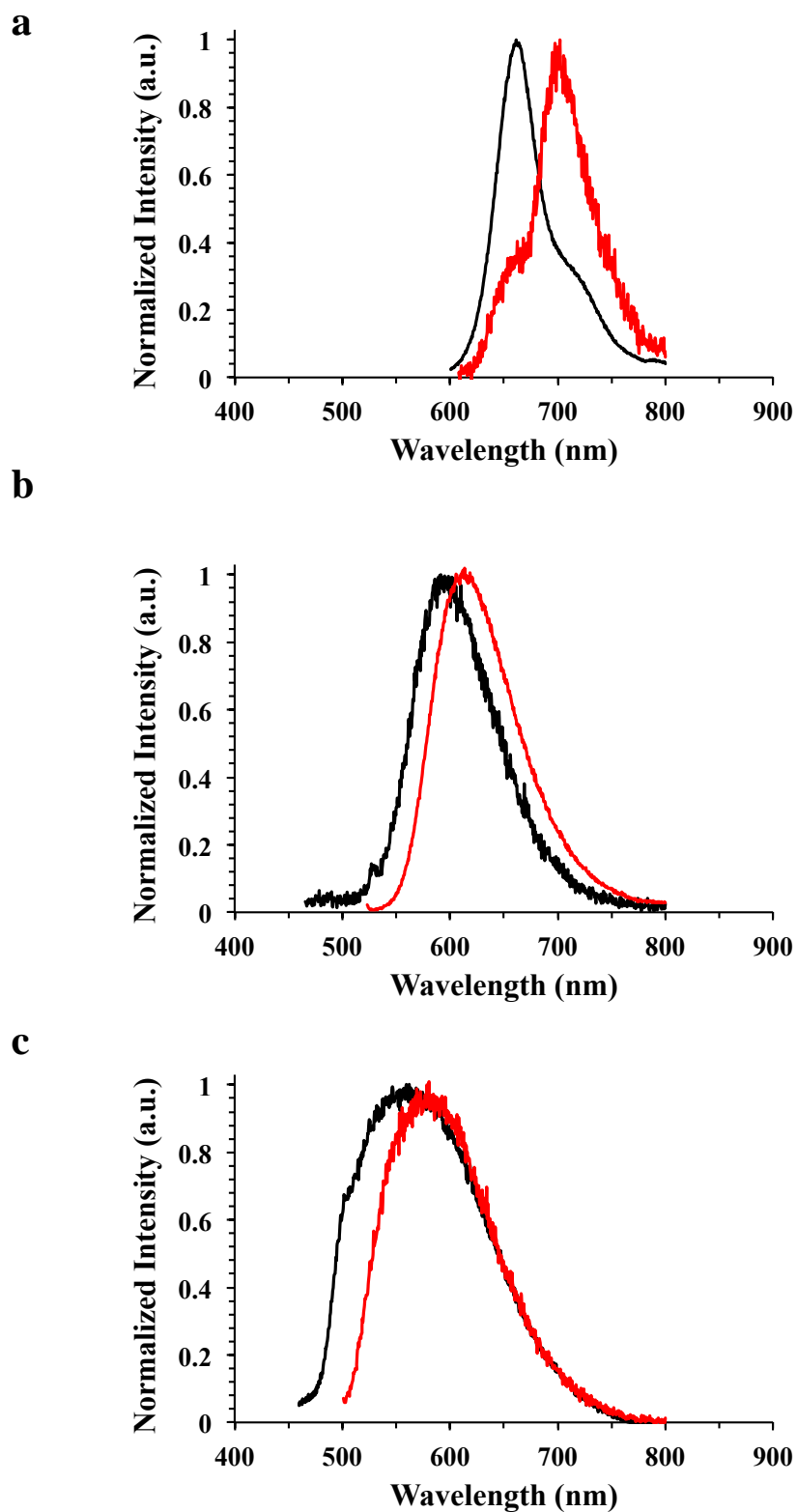
**Fig. S2**  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of 1,5-bis(2,6-dimethoxyphenyl)-3-cyanoformazan in  $\text{CDCl}_3$ . Asterisk denotes solvent signal.



**Fig. S3** <sup>1</sup>H NMR spectrum of BF<sub>2</sub> 3-cyanoformazanate **5c** in CDCl<sub>3</sub>.

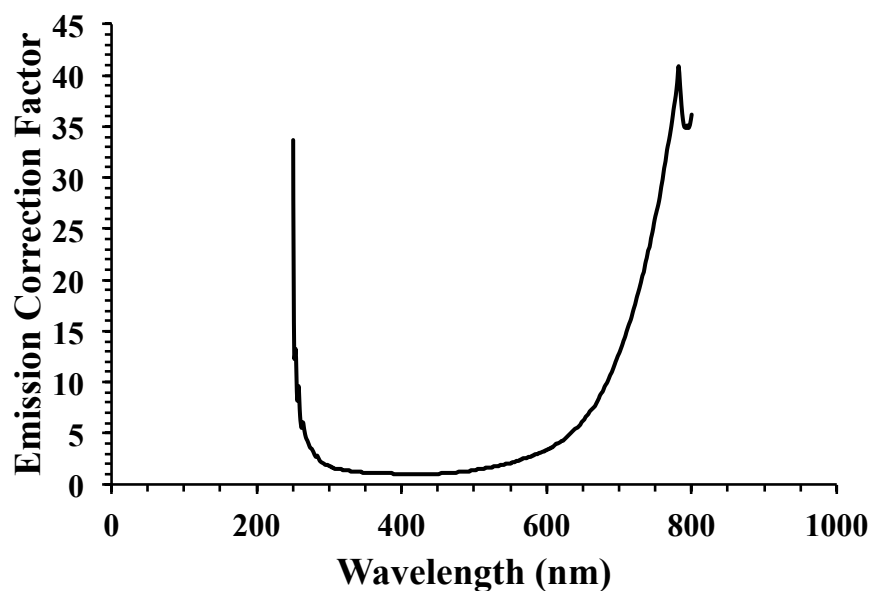


**Fig. S4** <sup>13</sup>C{<sup>1</sup>H} NMR spectrum of BF<sub>2</sub> 3-cyanoformazanate **5c** in CDCl<sub>3</sub>. Asterisk denotes solvent signal.

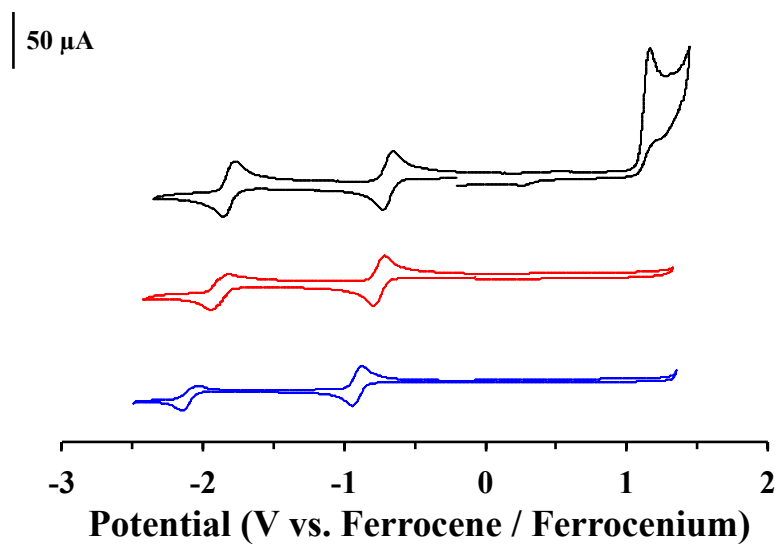


**Fig. S5** Normalized UV-vis emission spectra of **5a** (a), **5b** (b), and **5c** (c) in pure THF solution (black line; 250  $\mu$ M) and in a THF-water mixture ( $f_w = 95\%$ ; red line; 250  $\mu$ M).





**Fig. S6** Wavelength-dependent emission intensity correction provided by Photon Technology International.



**Fig. S7** Cyclic voltammograms of  $\text{BF}_2$  3-cyanoformazanates **5a** (Ar = 4-methoxyphenyl; black line), **5b** (Ar = 2-methoxyphenyl; red line), and **5c** (Ar = 2,6-dimethoxyphenyl; blue line) recorded in dry, degassed acetonitrile containing ~1 mM analyte and 0.1 M  $n\text{Bu}_4\text{NPF}_6$  at a scan rate of  $100 \text{ mV s}^{-1}$ .

**Table S2.** X-ray diffraction data collection and refinement details for **5c**.

	<b>5c</b>
Chemical Formula	C <sub>18</sub> H <sub>18</sub> BF <sub>2</sub> N <sub>5</sub> O <sub>4</sub>
Formula Weight (g mol <sup>-1</sup> )	417.18
Crystal Dimensions (mm)	0.311 × 0.309 × 0.177
Crystal Color and Habit	orange plate
Crystal System	orthorhombic
Space Group	<i>Pbca</i>
Temperature, (K)	110
<i>a</i> (Å)	14.740(3)
<i>b</i> (Å)	14.827(3)
<i>c</i> (Å)	18.170(4)
$\alpha$ (°)	90
$\beta$ (°)	90
$\gamma$ (°)	90
<i>V</i> (Å <sup>3</sup> )	3971.1(15)
<i>Z</i>	8
$\rho$ (g cm <sup>-3</sup> )	1.396
$\lambda$ (Å)	1.54178 (CuK $\alpha$ )
$\mu$ (cm <sup>-1</sup> )	0.957
Diffractometer Type	Nonius KappaCCD Apex2
<i>R</i> <sub>merge</sub>	0.0354
<i>R</i> <sub>1</sub> [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	0.0296
$\omega R_2$ [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	0.0740
<i>R</i> <sub>1</sub> (all data)	0.0313
$\omega R_2$ (all data)	0.0753
GOF	1.034

$$R_1 = \Sigma(|F_o| - |F_c|) / \Sigma F_o$$

$$\omega R_2 = [\Sigma(\omega(F_o^2 - F_c^2)^2) / \Sigma(\omega F_o^4)]^{1/2}$$

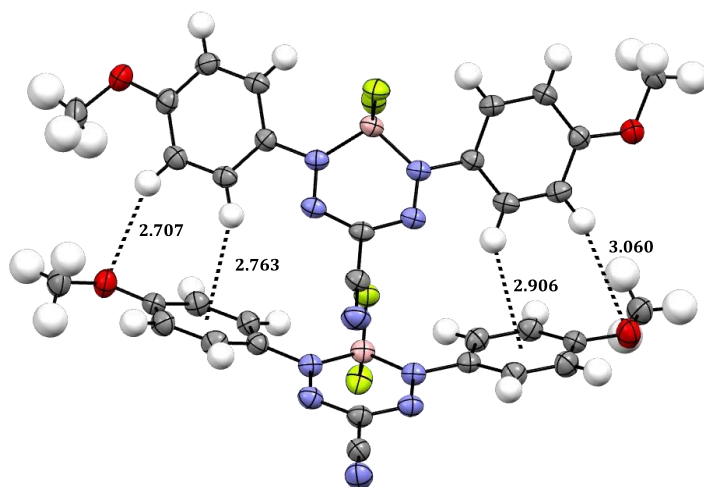
$$GOF = [\Sigma(\omega(F_o^2 - F_c^2)^2) / (\text{No. of reflns.} - \text{No. of params.})]^{1/2}$$

**Table S3.** Selected bond lengths (Å) and angles (°) for BF<sub>2</sub> 3-cyanoformazanate complexes **5a–c**.

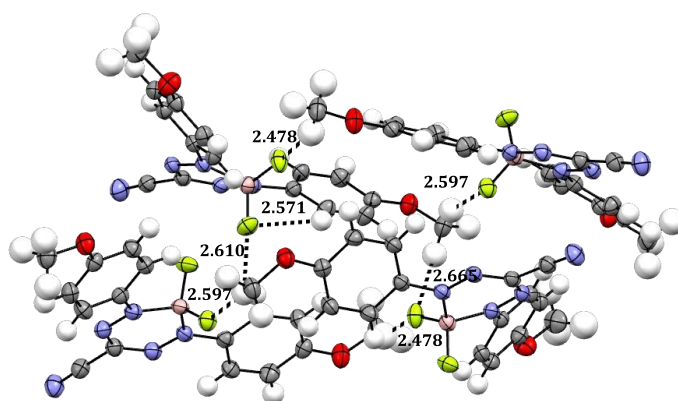
	<b>5a</b> <sup>a,1</sup>	<b>5b</b> <sup>2</sup>	<b>5c</b>	
N1-N2	1.307(2)	1.2987(6)	1.3040(16)	1.2980(13)
N3-N4	1.304(2)	–	1.3038(16)	1.2973(13)
C1-N2	1.340(3)	1.3443(5)	1.3404(19)	1.3435(15)
C1-N4	1.335(3)	–	1.3438(18)	1.3486(15)
N1-N2-C1	116.75(18)	116.42(4)	116.09(11)	114.50(9)
N1-B1-N3	106.85(17)	–	101.99(10)	100.14(8)
N1-B1-N1'	–	102.63(5)	–	–
N2-C1-N4	130.0(2)	–	126.85(12)	126.08(10)
N2-C1-N2'	–	127.22(6)	–	–
dihedral angles <sup>b</sup>	15.3, 21.4	47.7, 47.7	62.0, 60.5	74.6, 66.6

<sup>a</sup>The asymmetric unit determined for **5a** contains two unique molecules. <sup>1</sup><sup>b</sup>Dihedral angle between the N1 and N3 aryl substituents and the N<sub>4</sub> plane.

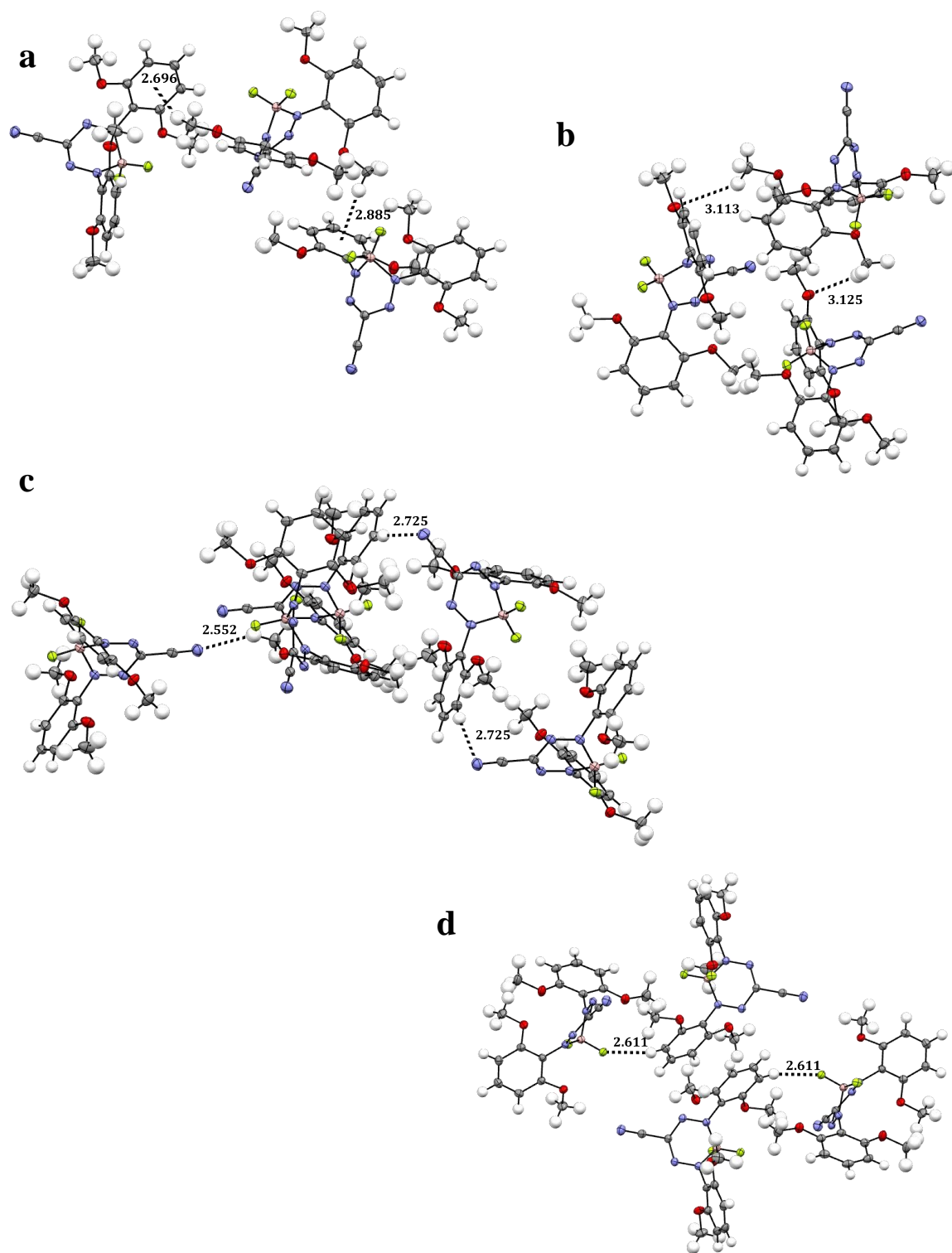
**a**



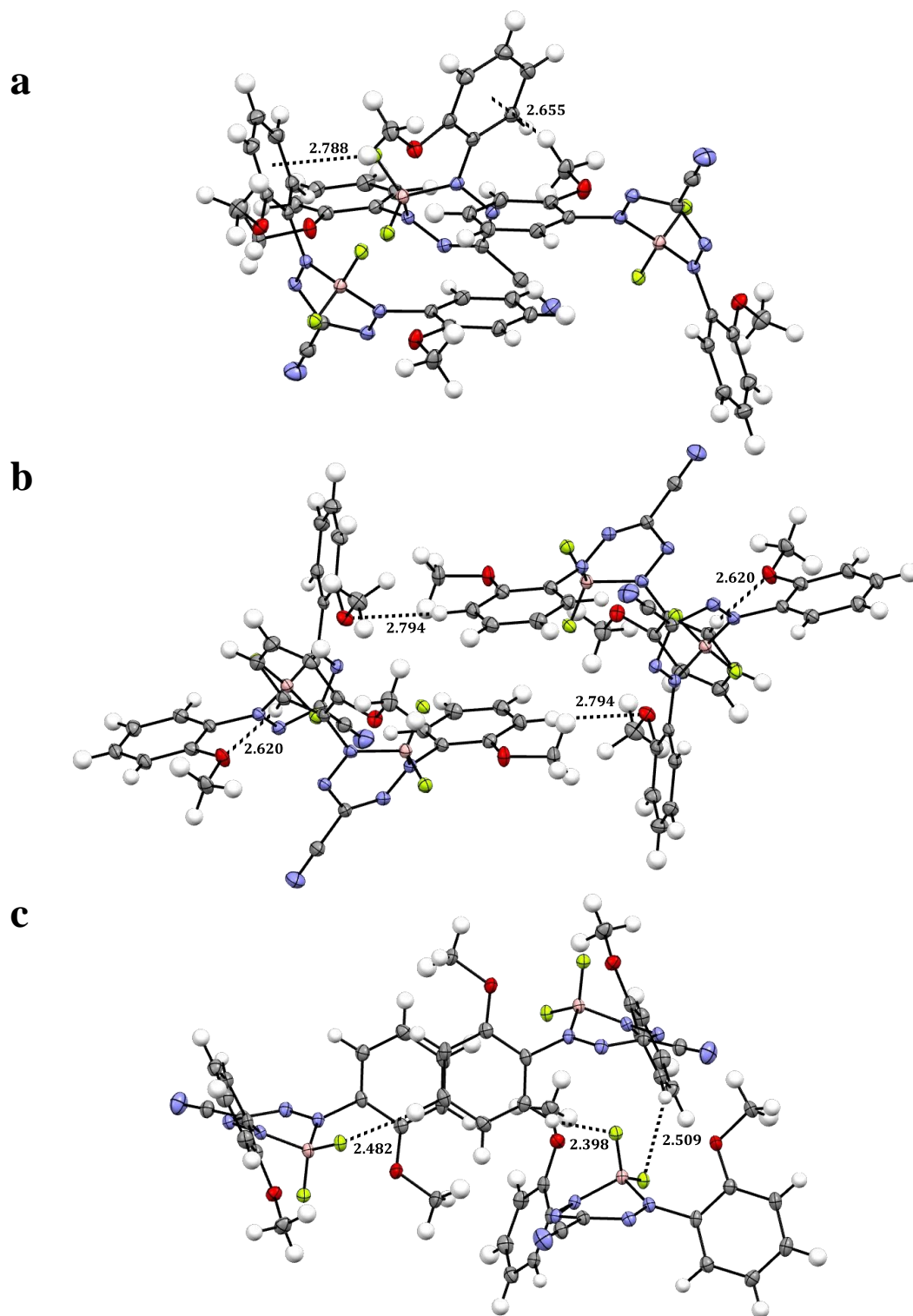
**b**



**Fig. S8** Intermolecular solid-state CH...O, CH... $\pi$  (a) and CH...F (b) interactions for **5a**. Anisotropic displacement ellipsoids are shown at 50% probability. All distances are quoted in Å.

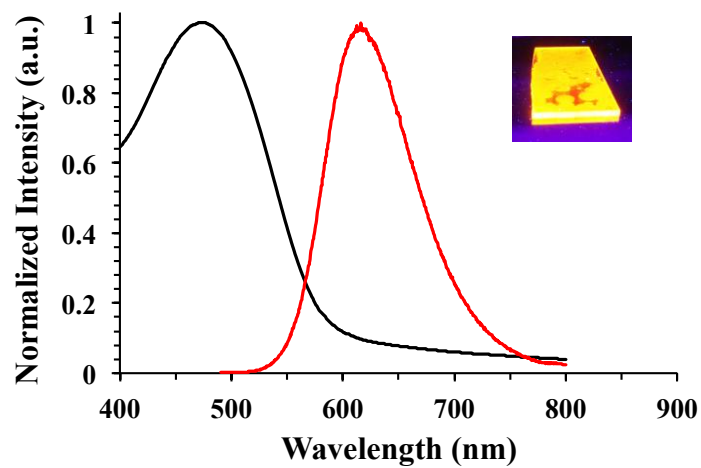


**Fig. S9** Intermolecular solid-state CH... $\pi$  (a), CH...O (b), CH...N (c), and CH...F (d) interactions for **5c**. Anisotropic displacement ellipsoids are shown at 50% probability. All distances are quoted in Å.

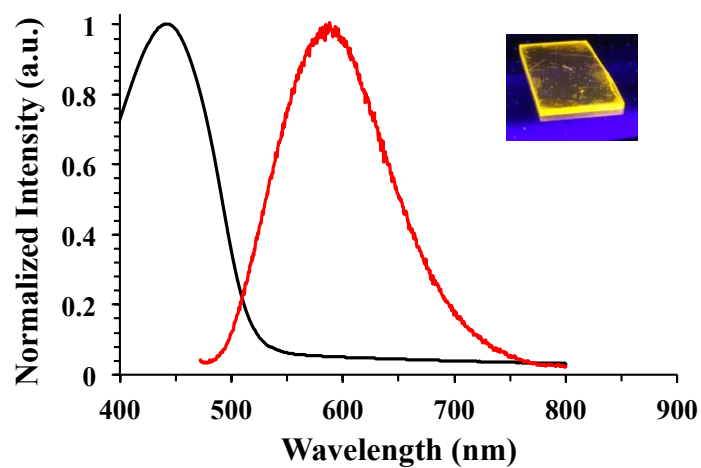


**Fig. S10** Intermolecular solid-state CH $\cdots\pi$  (a), CH $\cdots$ O (b), and CH $\cdots$ F (c) interactions for **5b**. Anisotropic displacement ellipsoids are shown at 50% probability. All distances are quoted in Å.

**a**



**b**



**Fig. S11** Normalized UV-vis absorption (black line) and emission (red line) spectra of thin films of **5b** (a) and **5c** (b). Insets provide a visual representation of the emission under UV irradiation (365 nm).

## References

- 1 S. M. Barbon, P. A. Reinkeluers, J. T. Price, V. N. Staroverov and J. B. Gilroy, *Chem. Eur. J.*, 2014, **20**, 11340.
- 2 R. R. Maar, S. M. Barbon, N. Sharma, H. Groom, L. G. Luyt and J. B. Gilroy, *Chem. Eur. J.*, 2015, **21**, 15589.
- 3 S. Fery-Forgues and D. Lavabre, *J. Chem. Educ.*, 1999, **76**, 1260.
- 4 Bruker-AXS, SAINT version 2013.8, **2013**, Bruker-AXS Madison, WI 53711, USA.
- 5 Bruker-AXS, SADABS version 2012.1, **2012**, Bruker-AXS, Madison, WI 53711, USA.
- 6 G. M. Sheldrick, *Acta Cryst.*, 2015, **A71**, 3.
- 7 G. M. Sheldrick, *Acta Cryst.*, 2008, **A64**, 112.
- 8 K. Suzuki, A. Kobayashi, S. Kaneko, K. Takehira, T. Yoshihara, H. Ishida, Y. Shiina, S. Oishi and S. Tobita, *Phys. Chem. Chem. Phys.*, 2009, **11**, 9850.