

## Supporting Information

### **Rigidly linked dinuclear platinum(II) complexes showing intense, excimer-like, near infra-red luminescence**

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# 1. General

## Calculations

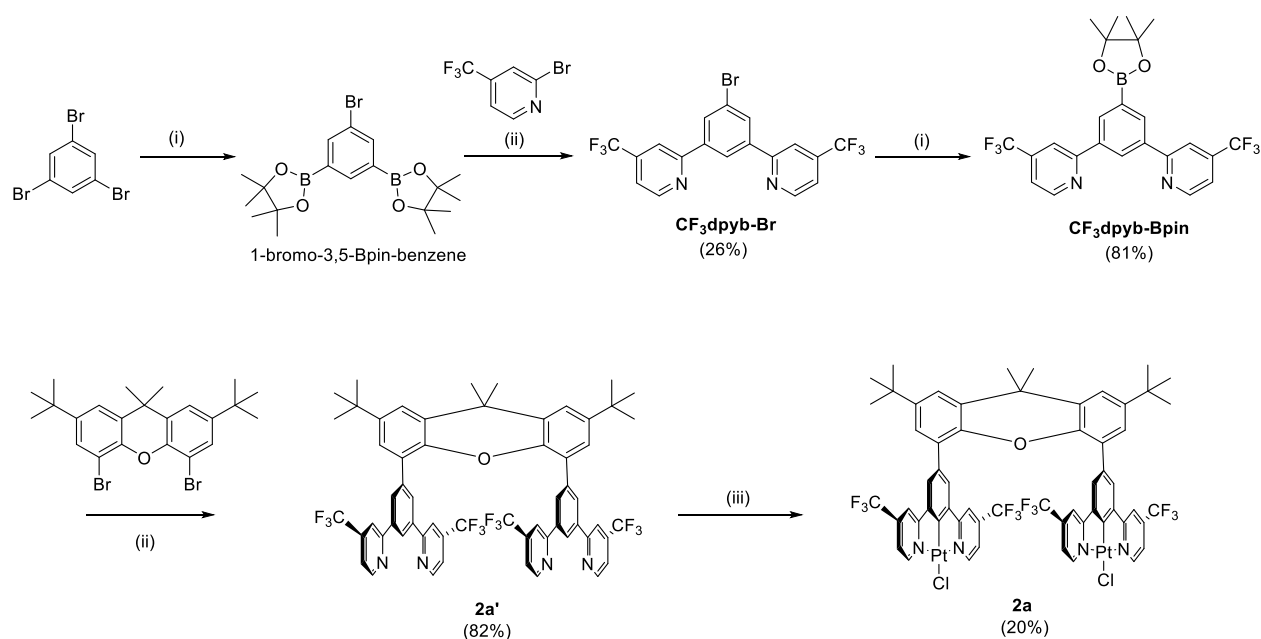
DFT/TD-DFT calculations were performed using Orca 4.2.1 software<sup>1-3</sup> and the results were visualised using Gabedit 2.5.0.<sup>4</sup> Ground state ( $S_0$ ) and triplet excited state ( $T_1$ ) geometry were calculated using the BP86<sup>5</sup> functional and the def2-svp<sup>6</sup> basis set for all atoms with effective core potential (ECP) for platinum. Single-point energy calculations were conducted using time-dependent density functional theory (TD-DFT) with the Tamm-Dancoff approximation (TDA), using the CAM-B3LYP<sup>7</sup> functional and the same basis set. Calculation time was greatly reduced using the RIJCOSX<sup>8,9</sup> approximation with def2/J<sup>10</sup> auxiliary Coulomb-fitting basis set, dense grid (Grid6, Gridx6), and tight SCF and geometry optimization criteria. The calculation uses atom-pairwise dispersion correction with the Becke-Johnson damping scheme (D3BJ).<sup>11,12</sup> All MO iso surfaces were rendered with iso value of 0.03 if not stated otherwise. All geometry optimisations were followed by vibrational frequency calculation to confirm minimal energy configurations.

## Photophysics

Absorption spectra of solutions were recorded with UV-3600 double beam spectrophotometer (Shimadzu). Photoluminescence (PL) spectra of solutions and films were recorded using a QePro compact spectrometer (Ocean Optics), or a FluoroMax-2 fluorescence spectrometer (Jobin Yvon). Time-resolved photoluminescence measurements in solution were recorded with an Horiba DeltaFlex TCSPC system using a 330 nm SpectraLED or a 405 nm Delta Diode light source. Solutions were degassed using 5 freeze-pump-thaw cycles.<sup>13</sup> Photoluminescence decays in film were recorded using nanosecond gated luminescence and lifetime measurements (from 400 ps to 1 s) using the third harmonic (355 nm) of a pulsed Nd:YAG laser (EKSPLA) as the excitation source. Temperature-dependent experiments in films were conducted using a liquid nitrogen cryostat VNF-100 (sample in flowing vapour, Janis Research) under nitrogen atmosphere, while measurements at room temperature were recorded under vacuum in the same cryostat.

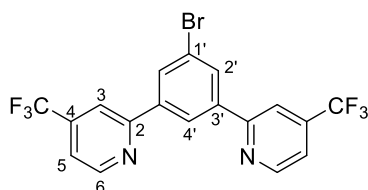
## 2. Synthesis

Compound **1a** was prepared as described previously.<sup>14</sup> Crystals of **1a** suitable for X-ray diffraction analysis were obtained in the present study from a methanol solution: see Section 3 below. Compound **2a** was prepared in a similar way as for **1a**, as illustrated in **Scheme S2.1**. The intermediate compound 2,2'-(5-bromo-1,3-phenylene)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) was prepared as described elsewhere,<sup>15</sup> and all other compounds are characterised below.



**Scheme S2.1** Synthetic route to **2a**. Reaction conditions: (i) Miyaura borylation: B<sub>2</sub>pin<sub>2</sub>, KOAc, Pd(dppf)Cl<sub>2</sub>, Dioxane, 80°C, 18 h; (ii) Suzuki coupling: Na<sub>2</sub>CO<sub>3</sub> (1 M, aq.), Pd(PPh<sub>3</sub>)<sub>4</sub>, DME, 85°C, 18 h; (iii) Complexation: K<sub>2</sub>PtCl<sub>4</sub>, acetic acid, 118°C, 1 week.

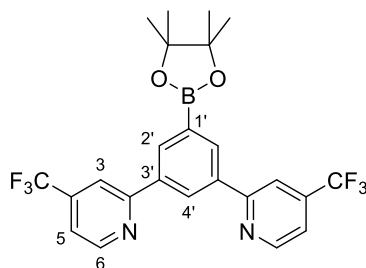
### CF<sub>3</sub>dpyb-Br



This compound was prepared *via* a Suzuki cross-coupling reaction. Crude 1,3-di(pinacolatoboron)-5-bromobenzene (2.59 g, 6.35 mmol), 2-bromo-4-(trifluoromethyl)-

pyridine (2.87 g, 0.013 mmol), and aqueous Na<sub>2</sub>CO<sub>3</sub> (5.39 g, 50.8 mmol) were added with DME (25 mL) to a Schlenk tube and degassed by three freeze-pump-thaw cycles. The catalyst Pd(PPh<sub>3</sub>)<sub>4</sub> (0.367 g, 0.318 mmol) was added and the reaction mixture heated at 85°C for 18 h under an atmosphere of nitrogen. On cooling to room temperature, the mixture was extracted with CH<sub>2</sub>Cl<sub>2</sub>, the extracts dried over anhydrous magnesium sulphate, and the solvent removed under reduced pressure. The crude mixture was purified by column chromatography on silica (hexane: ethyl acetate gradient, R<sub>f</sub> = 0.4 in 90:10) to yield the title compound as a white solid (0.740 g, 26%); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ<sub>H</sub> = 8.95 (2 H, d, J 5.0, H<sup>6</sup>), 8.68 (1 H, t, J 1.6, H<sup>4'</sup>), 8.33 (2 H, d, J 1.6, H<sup>2'</sup>), 8.06 (2 H, dt, J 1.7, 0.8, H<sup>3</sup>), 7.57 (2 H, dt, J 4.9, 1.3, H<sup>5</sup>); <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) δ<sub>F</sub> = -64.7; MS ESI (ES<sup>+</sup>) *m/z* 447.0 ([M+H]<sup>+</sup>, 100%); HRMS (ES<sup>+</sup>) *m/z* 446.9937 [M+H]<sup>+</sup>, calc. for [C<sub>18</sub>H<sub>10</sub>N<sub>2</sub>BrF<sub>6</sub>N<sub>2</sub>] 446.9932.

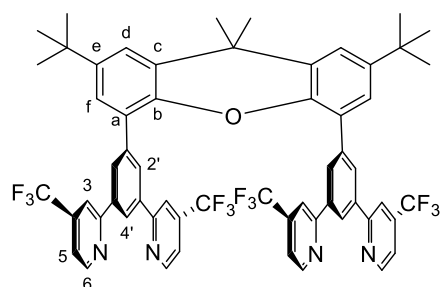
### CF<sub>3</sub>dypb-Bpin



This compound was prepared *via* a Miyaura borylation reaction. CF<sub>3</sub>dypb-Br (340 mg, 0.762 mmol), B<sub>2</sub>pin<sub>2</sub> (233 mg, 0.915 mmol), and KOAc (449 mg, 4.57 mmol) were added to a Schlenk tube with dry 1,4-dioxane (10 mL) and degassed by three freeze-pump-thaw cycles. The catalyst PdCl<sub>2</sub>(dppf) (56 mg, 0.076 mmol) was added and the reaction mixture heated at 85°C overnight under an atmosphere of nitrogen. The crude mixture was filtered and washed with CH<sub>2</sub>Cl<sub>2</sub>. Purification by flash column chromatography (hexane: ethyl acetate on silica, R<sub>f</sub> = 0.3 in 80:20) yielded the product as a white solid (305 mg, 81%); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ<sub>H</sub> = 9.00 – 8.86 (3 H, m, H<sup>6</sup> and H<sup>4'</sup>), 8.53 (2 H, d, J 1.9, H<sup>2'</sup>), 8.11 (2 H, dt, J 1.5, 0.8, H<sup>3</sup>), 7.51 (2 H, ddd, J 5.0, 1.6, 0.8, H<sup>5</sup>), 1.43 (12 H, s, H<sup>Bpin</sup>); MS ESI (ES<sup>+</sup>) *m/z* 495.4 ([M+H]<sup>+</sup>, 100%); HRMS (ES<sup>+</sup>) *m/z* 494.1709 [M+H]<sup>+</sup>, calc. for [C<sub>24</sub>H<sub>22</sub>N<sub>2</sub>O<sub>2</sub><sup>10</sup>BF<sub>6</sub>] 494.1715.

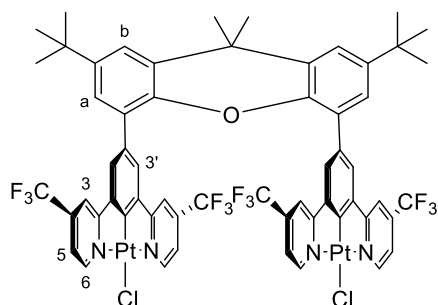


## Compound **2a'**



This compound was prepared *via* a Suzuki cross-coupling reaction as described for **CF<sub>3</sub>dpyb-Br** but using crude **CF<sub>3</sub>dpyb-Bpin** (754 mg, 1.53 mmol), 4,5-dibromo-2,7-di-*tert*-butyl-9,9-dimethylxanthene (333 mg, 0.693 mmol), aqueous Na<sub>2</sub>CO<sub>3</sub> (588 mg, 5.54 mmol), Pd(PPh<sub>3</sub>)<sub>4</sub> (40 mg, 0.035 mmol) and DME (6 mL). The crude mixture was purified by column chromatography on silica (hexane: ethyl acetate gradient, R<sub>f</sub> = 0.2 in 90:10) to yield the title compound as a white solid (603 mg, 82%); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ<sub>H</sub> = 8.70 (4 H, d, J 5.0, H<sup>6</sup>), 8.24 (2 H, t, J 1.7, H<sup>4'</sup>), 7.99 (4 H, d, J 1.7, H<sup>2'</sup>), 7.68 (4 H, d, J 1.5, H<sup>3</sup>), 7.55 (2 H, d, J 2.3, H<sup>f</sup>), 7.26 – 7.23 (2 H, m, H<sup>d</sup>), 7.14 (4 H, dd, J 5.0, 1.5, H<sup>5</sup>), 1.87 (6 H, s, H<sup>Me</sup>), 1.40 (18 H, s, H<sup>tBu</sup>); MS ESI (ES<sup>+</sup>) *m/z* 1053.9 (M<sup>+</sup>, 82%).

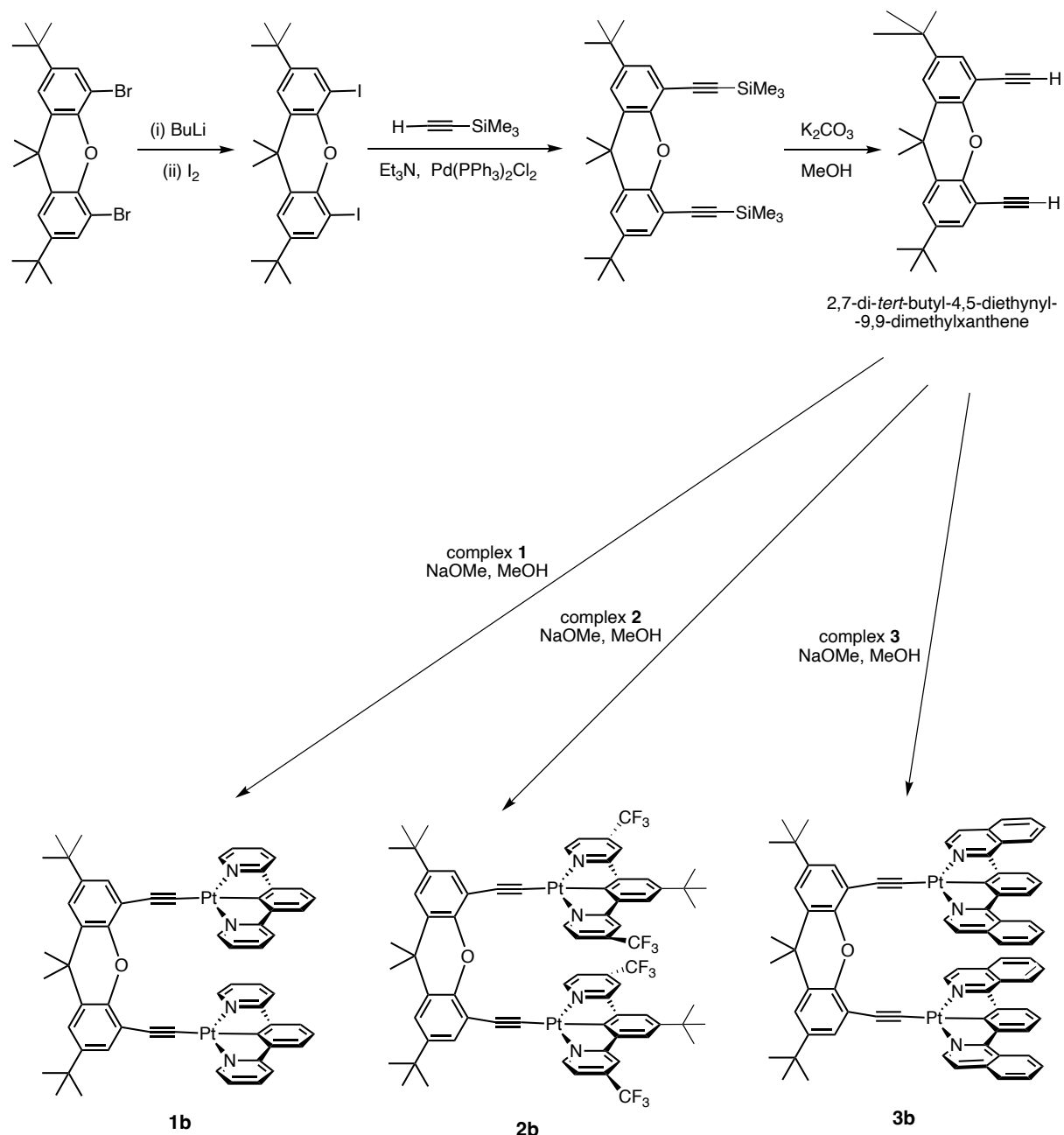
## Compound **2a**



Potassium tetrachloroplatinate(II) (98 mg, 0.237 mmol) was added to a solution of **2a'** (50 mg, 0.047 mmol) in acetic acid (10 mL) in a dry Schlenk flask and the solution was degassed using three freeze-pump-thaw cycles. The reaction mixture was then heated at reflux (118°C) for 60 h under nitrogen before cooling to room temperature. The crude solid was purified by preparative column chromatography on silica (DCM: MeOH gradient) to yield the target dinuclear complex **2a** as a yellow-orange solid (6.5 mg, 9%); <sup>1</sup>H NMR (700 MHz, CDCl<sub>3</sub>) δ<sub>H</sub>

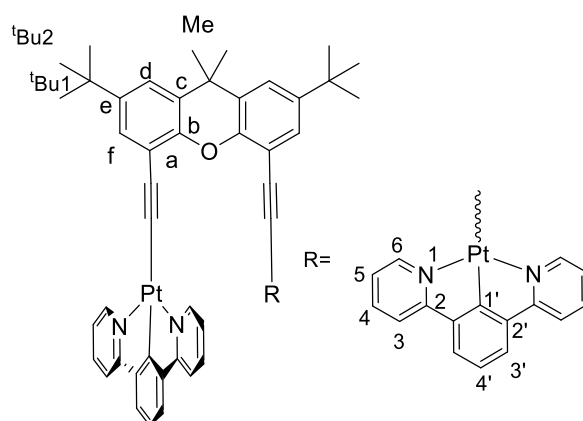
= 9.53 (4 H, d, J 5.8, {<sup>195</sup>Pt 32}, H<sup>6</sup>), 7.54 (2 H, d, J 2.4, H<sup>d</sup> or H<sup>f</sup>), 7.48 (4 H, s, H<sup>2'</sup>), 7.41 (4 H, s, H<sup>3</sup>), 7.38 (4 H, dd, J 5.8, 1.9, H<sup>5</sup>), 7.22 (2 H, d, J 2.3, H<sup>d</sup> or H<sup>f</sup>), 1.83 (6 H, s, H<sup>Me</sup>), 1.41 (18 H, s, H<sup>t-Bu</sup>); <sup>13</sup>C NMR (176 MHz, CDCl<sub>3</sub>) δ<sub>C</sub> = 167.9 (C<sup>2</sup>), 161.8 (C<sup>4'</sup>), 154.0 (C<sup>6</sup>), 146.2 (C<sup>e</sup>), 144.1 (C<sup>b</sup>), 139.3 (C<sup>1'</sup>), 129.3 (C<sup>e</sup>), 128.1 (C<sup>a</sup>), 126.7 (C<sup>2'</sup>), 125.8 (C<sup>d</sup> or C<sup>f</sup>), 123.3 (C<sup>d</sup> or C<sup>f</sup>), 119.6 (C<sup>5</sup>), 115.1 (C<sup>3</sup>), 34.7 (C<sup>g</sup>), 34.1 (C<sup>t-Bu</sup>), 33.7 (C<sup>Me</sup>); <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) δ<sub>F</sub> = -65.54; MS ESI (ES<sup>+</sup>) *m/z* 1555.7 [M+MeCN]<sup>+</sup>; HRMS ASAP (AP<sup>+</sup>) *m/z* 1477.8969 [M-Cl]<sup>+</sup>, calc. for [C<sub>59</sub>H<sub>44</sub>ClF<sub>12</sub>N<sub>4</sub>OPt<sub>2</sub>] 1478.2312; Anal. Calc. for C<sub>59</sub>H<sub>44</sub>Cl<sub>2</sub>F<sub>12</sub>N<sub>4</sub>OPt<sub>2</sub>: C, 46.8; H, 2.93; N, 3.50 %. Found: C, 46.90; H, 3.10; N, 3.50 %.

Compounds **1b**, **2b**, and **3b** were obtained from their respective mononuclear counterparts **1**, **2**, and **3** using the procedure illustrated in **Scheme S2.2**. Complexes **1**, **2** and **3** were obtained as described elsewhere.<sup>16–18</sup> The intermediate 2,7-di-*tert*-butyl-4,5-diethynyl-9,9-dimethylxanthene was synthesised following a previously reported procedure.<sup>19</sup>



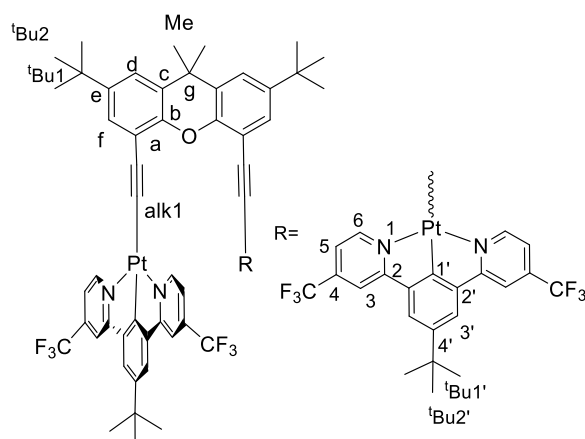
**Scheme S2.2** Synthetic route to the acetylide linked dinuclear compounds **1b**, **2b**, and **3b**.

## Compound 1b



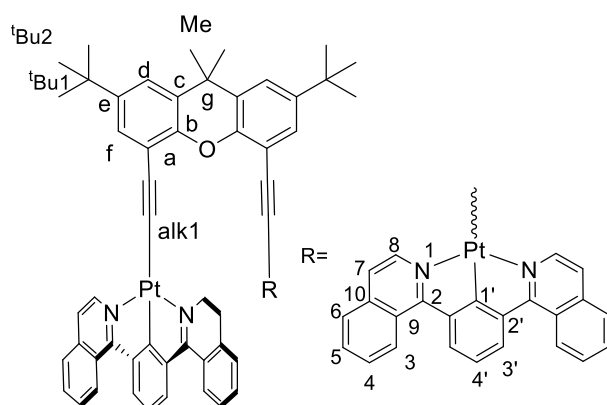
2,7-Di-tert-butyl-4,5-diethynyl-9,9-dimethylxanthene (7.5 mg, 0.02 mmol, prepared as described in earlier literature<sup>19</sup>) and a solution of NaOMe in MeOH (5 M, 1 mL, 0.05 mmol) were added to MeOH (15 mL) in a Schlenk tube under nitrogen. A solution of Pt(dpyb)Cl, **1**, (18 mg, 0.04 mmol) in DCM (15 mL) was then added. The mixture was stirred at 60°C for 48 h. On cooling to ambient temperature, the solvent was removed under reduced pressure and the resulting orange solid was washed with H<sub>2</sub>O, MeOH and Et<sub>2</sub>O. Recrystallisation from DCM / *n*-hexane gave the desired product (10 mg, 41 %); <sup>1</sup>H NMR (700 MHz, Chloroform-*d*) δ<sub>H</sub> = 9.51 (d, *J* = 5.5 Hz, 4H, H<sup>6</sup>), 7.47 – 7.44 (m, 6H, H<sup>d/f</sup> and H<sup>4</sup>), 7.24 (d, *J* = 2.4 Hz, 2H, H<sup>d/f</sup>), 7.08 (dd, *J* = 7.8, 1.3 Hz, 4H, H<sup>3</sup>), 6.97 – 6.93 (m, 8H, H<sup>3'</sup> and H<sup>5</sup>), 6.85 (t, *J* = 7.5 Hz, 2H, H<sup>4'</sup>), 1.70 (s, 6H, H<sup>Me</sup>), 1.33 (s, 18H, H<sup>tBu2</sup>); <sup>13</sup>C NMR (176 MHz, CDCl<sub>3</sub>) δ<sub>C</sub> = 168.8 (C<sup>2</sup>), 156.8 (C<sup>6</sup>), 143.9 (C<sup>e</sup>), 142.3 (C<sup>2'</sup>), 136.7 (C<sup>d/f</sup>), 128.9 (C<sup>c</sup>), 128.1 (C<sup>4</sup>), 122.8 (C<sup>3'</sup>), 122.8 (C<sup>5</sup>), 121.5 (C<sup>4'</sup>), 119.4 (C<sup>d/f</sup>), 118.1 (C<sup>3</sup>), 34.7 (C<sup>g</sup>), 34.4 (C<sup>tBu1</sup>), 32.6 (C<sup>Me</sup>), 31.6 (C<sup>tBu2</sup>); MS (ASAP<sup>+</sup>) *m/z* = 1221.3 [M+H]<sup>+</sup>; HRMS (ASAP<sup>+</sup>) *m/z* = 1221.3357 [M+H]<sup>+</sup>; calculated for [C<sub>59</sub>H<sub>51</sub>N<sub>4</sub>O<sup>194</sup>Pt<sub>2</sub>]<sup>+</sup> 1221.3331. Anal. calc. for C<sub>60</sub>H<sub>53</sub>N<sub>4</sub>OCl<sub>2</sub>Pt<sub>2</sub>: 55.13; H, 4.09; N 4.29 %; found C, 55.49; H, 4.15; N 3.91 %.

## Compound 2b



The complex was prepared using the same procedure as **1b**, but using **2** in place of **1**. The complex was obtained as a dark red solid in 73 % yield;  $^1\text{H}$  NMR (700 MHz, Chloroform-*d*)  $\delta_{\text{H}} = 9.60$  (d,  $J = 5.8$  Hz, 4H, H<sup>6</sup>), 7.39 (d,  $J = 2.3$  Hz, 2H, H<sup>d/f</sup>), 7.30 (d,  $J = 2.3$  Hz, 2H, H<sup>d'/f'</sup>), 7.25 (s, 4H, H<sup>3</sup>), 7.18 (d,  $J = 5.2$  Hz, 4H, H<sup>5</sup>), 7.11 (s, 4H, H<sup>3'</sup>), 1.74 (s, 6H, H<sup>Me</sup>), 1.40 (s, 18H, H<sup>tBu2'</sup>), 1.35 (s, 18H, H<sup>tBu2</sup>);  $^{13}\text{C}$  NMR (176 MHz, Chloroform-*d*)  $\delta_{\text{C}} = 178.6$  (C<sup>1'</sup>), 169.9 (C<sup>2'</sup>), 157.9 (C<sup>6</sup>), 150.3 (C<sup>b</sup>), 145.5 (C<sup>4'</sup>), 144.5 (C<sup>e</sup>), 140.7 (C<sup>2</sup>), 129.4 (C<sup>g</sup>), 127.1 (C<sup>d/f</sup>), 121.9 (C<sup>4</sup>), 121.4 (C<sup>3'</sup>), 119.7 (C<sup>d'/f'</sup>), 119.0 (C<sup>5</sup>), 116.0 (C<sup>alk1</sup>), 114.3 (C<sup>3</sup>), 35.2 (C<sup>tBu1'</sup>), 34.5 (C<sup>tBu1</sup>), 31.9 (C<sup>Me</sup>), 31.7 (C<sup>tBu2'</sup>), 31.6 (C<sup>tBu2</sup>);  $^{19}\text{F}$  NMR (376 MHz, CDCl<sub>3</sub>)  $\delta_{\text{F}} = -65.01$ ; MS (ASAP<sup>+</sup>)  $m/z = 1605.4$  [M+H]<sup>+</sup>; HRMS (ASAP<sup>+</sup>)  $m/z = 1605.4097$  [M+H]<sup>+</sup>; calculated for [C<sub>71</sub>H<sub>63</sub>N<sub>4</sub>O<sub>1</sub>F<sub>12</sub><sup>194</sup>Pt<sub>2</sub>]<sup>+</sup> 1605.4105.

## Compound 3b



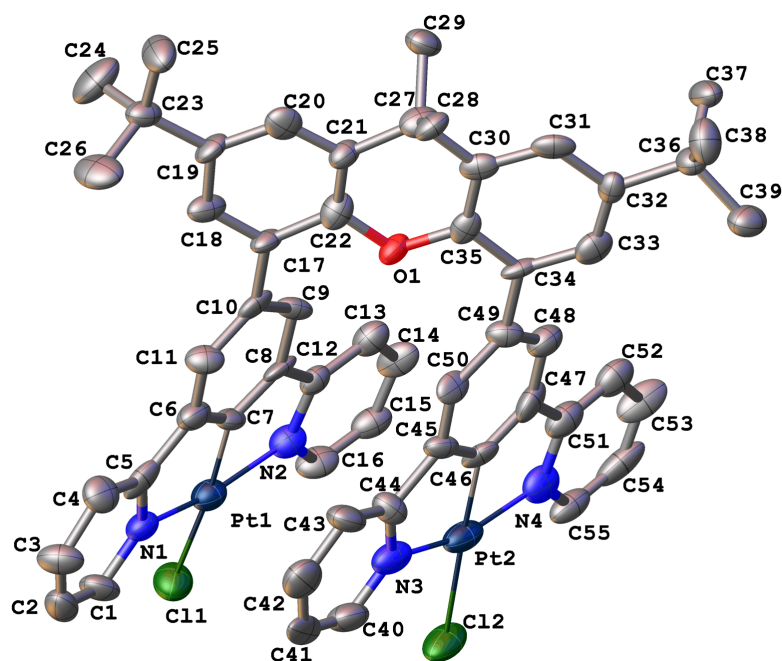
This compound was prepared using the same procedure as **1b**, but using **3** in place of **1**. The material was obtained as a dark red solid in 35 % yield.  $^1\text{H}$  NMR (700 MHz, CDCl<sub>3</sub>)  $\delta_{\text{H}} = 9.67$  (d,  $J = 6.2$  Hz, 4H, H<sup>8</sup>), 8.34 (d,  $J = 8.5$  Hz, 4H, H<sup>6</sup>), 7.68 (d,  $J = 7.8$  Hz, 4H, H<sup>3'</sup>), 7.54 (d,  $J =$

2.3 Hz, 2H, H<sup>d/f</sup>), 7.40 (d,  $J = 7.9$  Hz, 4H, H<sup>3</sup>), 7.35 (ddd,  $J = 7.9, 6.6, 1.0$  Hz, 4H, H<sup>4</sup>), 7.30 (d,  $J = 2.4$  Hz, 2H, H<sup>d/f</sup>), 7.28 (ddd,  $J = 8.1, 6.6, 1.4$  Hz, 4H, H<sup>5</sup>), 7.14 (d,  $J = 6.2$  Hz, 4H, H<sup>7</sup>), 7.00 (t,  $J = 7.7$  Hz, 2H, H<sup>4'</sup>), 1.77 (s, 6H, H<sup>Me</sup>), 1.37 (s, 18H H<sup>tBu2</sup>); <sup>13</sup>C NMR (176 MHz, CDCl<sub>3</sub>)  $\delta_C = 186.7$  (C<sup>1</sup>), 167.6 (C<sup>2</sup>), 148.8 (C<sup>8</sup>), 144.0 (C<sup>2'</sup>), 144.0 (C<sup>e</sup>), 136.4 (C<sup>9</sup>), 129.9 (C<sup>4</sup>), 129.0 (C<sup>g</sup>), 128.2 (C<sup>f/d</sup>), 127.8 (C<sup>3'</sup>), 127.2 (C<sup>3</sup>), 127.0 (C<sup>5</sup>), 126.1 (C<sup>10</sup>), 125.1 (C<sup>6</sup>), 121.2 (C<sup>4'</sup>), 121.1 (C<sup>7</sup>), 119.6 (C<sup>d/f</sup>), 34.4 (C<sup>tBu1</sup>), 32.7 (C<sup>Me</sup>), 31.6 (C<sup>tBu2</sup>). Anal. calc. for C<sub>75</sub>H<sub>58</sub>N<sub>4</sub>OPt<sub>2</sub>: 63.77; H, 4.11; N 3.94 %; found C, 64.05; H, 4.29; N 3.71 %. Crystals of this compound suitable for X-ray diffraction analysis (see Section 3 below) were obtained by diffusion of hexanes into a solution of the compound in CH<sub>2</sub>Cl<sub>2</sub>.

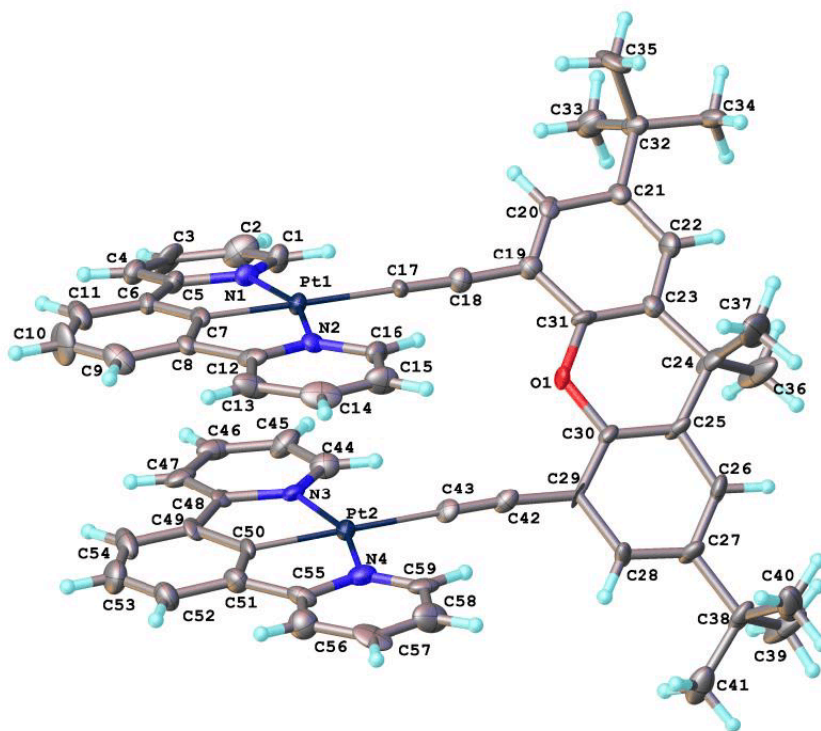
### 3. Crystallography

The X-ray single crystal data have been collected on a Bruker D8Venture (Photon100 CMOS detector,  $I\mu$ S-microsource, focusing mirrors) diffractometer equipped with a Cryostream (Oxford Cryosystems) open-flow nitrogen cryostat at the temperature 120.0(2) K using  $\lambda$ MoK $\alpha$  (compounds **1b** and **2**) or  $\lambda$ CuK $\alpha$  (compound **1a**) radiation ( $\lambda = 0.71073\text{\AA}$  and  $1.54178\text{\AA}$  respectively). The data for compound **3b** were collected at 100.0(2) K at I-19 beamline (Dectris Pilatus 2M pixel-array photon-counting detector, undulator, graphite monochromator,  $\lambda = 0.6889\text{\AA}$ ) at the Diamond Light Source, Oxfordshire and processed using Bruker APEXIII software.

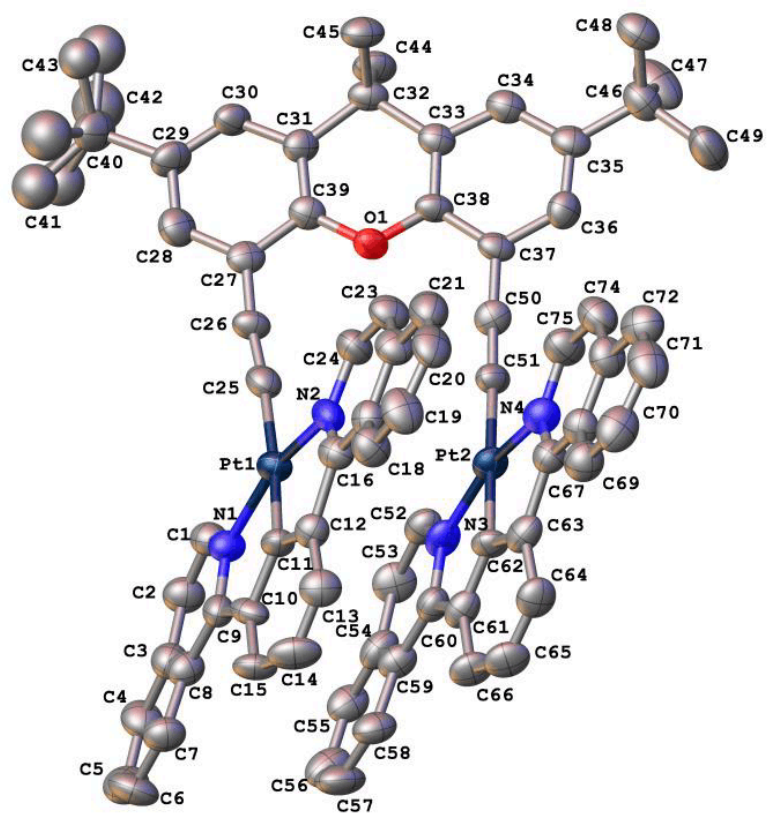
All structures were solved by direct methods and refined by full-matrix least squares on  $F^2$  for all data using Olex2<sup>20</sup> and SHELXTL<sup>21</sup> software. All non-hydrogen atoms were refined in anisotropic approximation, hydrogen atoms were placed in the calculated positions and refined in riding mode. The severely disordered solvent molecule in structure **1b** could not be successfully modelled and was taken into account by applying MASK procedure of Olex2 software package (55 independent electrons corresponding to a chloroform molecule). Crystal data and parameters of refinement are listed in **Table S1** below. Crystallographic data for the structures have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications CCDC 2063389, 2063391, 2063392.



**Figure S3.1.** The molecular structure of **1a**, including the atom numbering scheme.



**Figure S3.2.** The molecular structure of **1b**, including the atom numbering scheme.



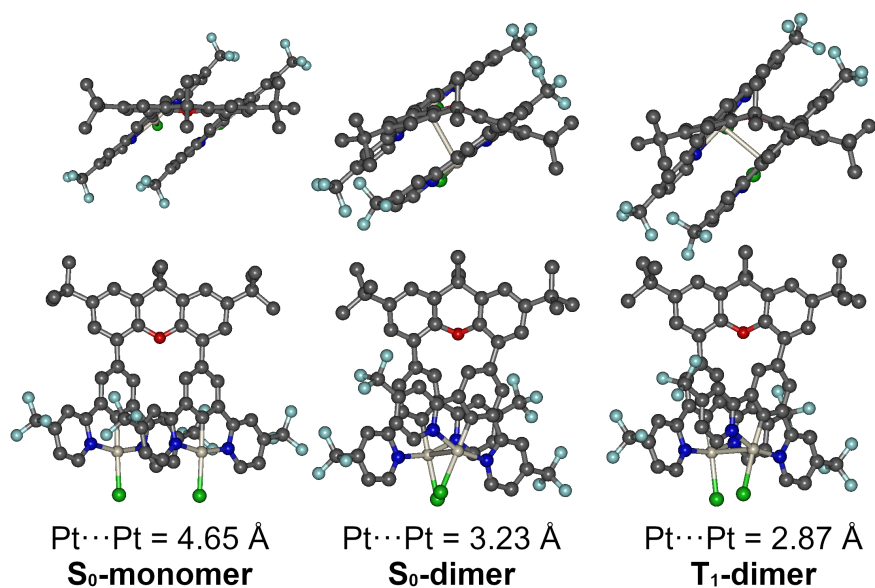
**Figure S3.3.** The molecular structure of **3b**, including the atom numbering scheme.



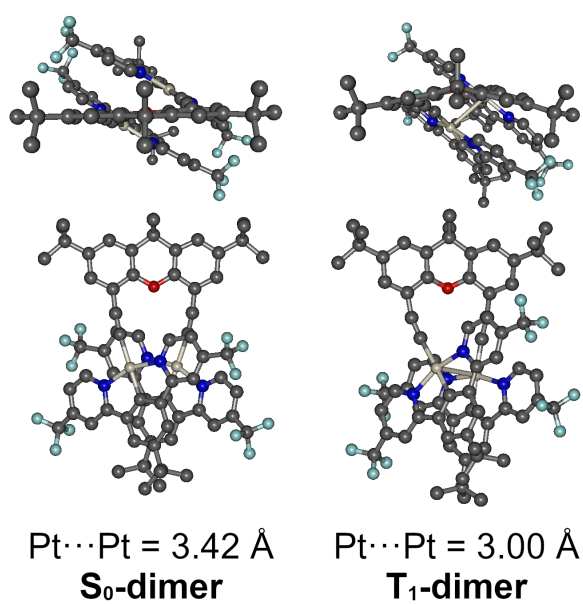
**Table S3.1.** Crystal data and structure refinement parameters

Compound	<b>1a</b>	<b>1b</b>	<b>3b</b>
Empirical formula	C <sub>56</sub> H <sub>52</sub> Cl <sub>2</sub> N <sub>4</sub> O <sub>2</sub> Pt <sub>2</sub>	C <sub>60</sub> H <sub>51</sub> Cl <sub>3</sub> N <sub>4</sub> OPt <sub>2</sub>	C <sub>75</sub> H <sub>58</sub> N <sub>4</sub> OPt <sub>2</sub>
Formula weight	1274.09	1340.57	1421.43
Temperature/K	120.0	120.0	100.0
Crystal system	monoclinic	monoclinic	triclinic
Space group	P2 <sub>1</sub> /c	P2 <sub>1</sub> /c	P-1
a/Å	15.1276(13)	11.1103(8)	12.3705(16)
b/Å	27.580(2)	26.454(2)	14.832(2)
c/Å	11.1881(9)	36.437(3)	17.645(2)
$\alpha$ /°	90	90	65.796(3)
$\beta$ /°	93.815(5)	96.037(3)	87.028(3)
$\gamma$ /°	90	90	73.841(3)
Volume/Å <sup>3</sup>	4657.6(7)	10649.9(14)	2829.0(7)
Z	4	8	2
$\rho_{\text{calc}}/\text{cm}^3$	1.817	1.672	1.669
$\mu/\text{mm}^{-1}$	12.508	5.444	4.596
F(000)	2488.0	5232.0	1400.0
Crystal size/mm <sup>3</sup>	0.08 × 0.04 × 0.005	0.22 × 0.18 × 0.09	0.025 × 0.015 × 0.005
Reflections collected	53291	151553	38279
Independent reflections, R <sub>int</sub>	8467, 0.2391	28121, 0.0752	13486, 0.0885
Data/restraints/parameters	8467/0/597	28121/66/1277	13486/15/741
Goodness-of-fit on F <sup>2</sup>	0.961	1.133	0.981
Final R <sub>1</sub> indexes [ $I \geq 2\sigma(I)$ ]	0.0721	0.0841	0.0864
Final wR <sub>2</sub> indexes [all data]	0.1808	0.1791	0.2684
CCDC number	2063389	2063391	2063392

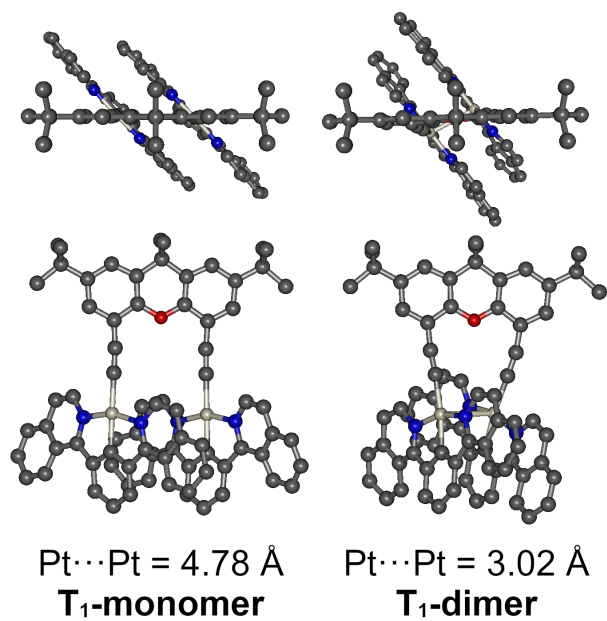
## 4. Calculations



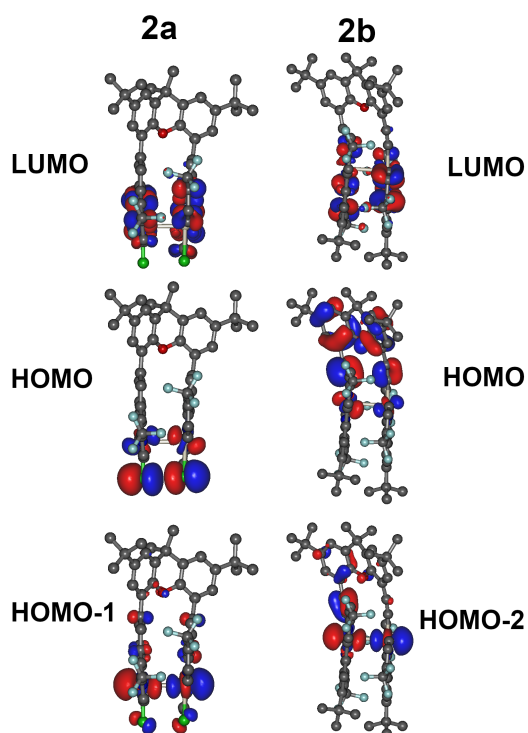
**Figure S4.1.** Optimised ground ( $S_0$ ) and triplet excited state ( $T_1$ ) geometries of **2a**.



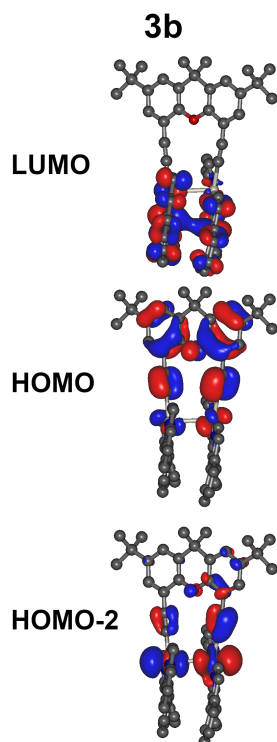
**Figure S4.2.** Optimised ground ( $S_0$ ) and triplet excited state ( $T_1$ ) geometries of **2b**.



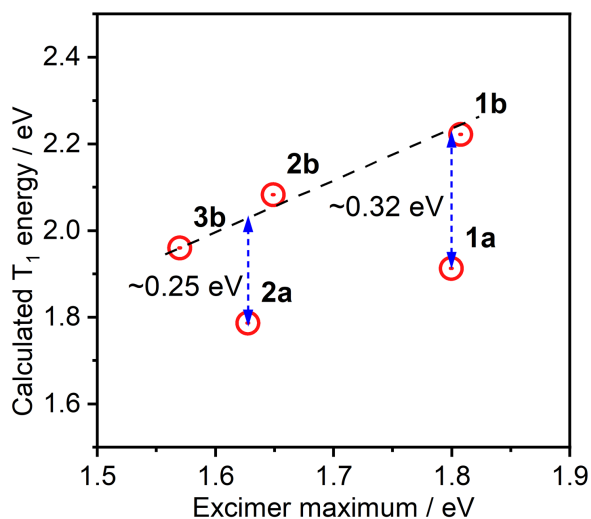
**Figure S4.3.** Optimised ground ( $S_0$ ) and triplet excited state ( $T_1$ ) geometries of **3b**.



**Figure S4.4.** Molecular orbital iso surfaces relevant to the  $T_1$ -dimer excited state of molecules **2a** and **2b**.



**Figure S4.5.** Molecular orbital iso surfaces relevant to the  $T_1$ -dimer excited state of molecule **3b**.

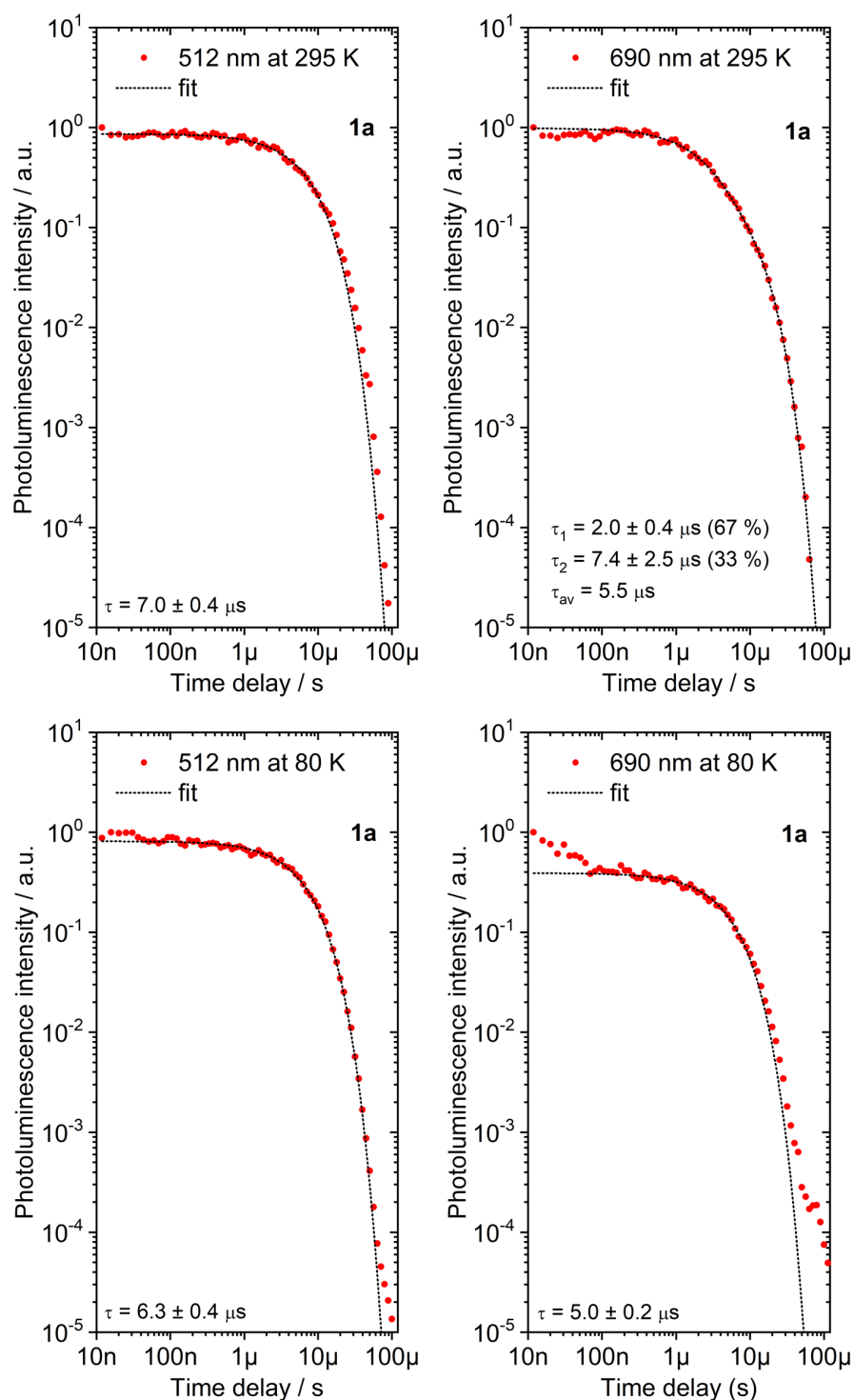


**Figure S4.6.** Relationship between the calculated  $T_1$  energy of the  $T_1$ -dimer structures of complexes **1a**, **2a**, **1b-3b** and PL maxima of the excimer-like emission. Black dashed line serves as an eye-guide for the molecules **1b-3b**.

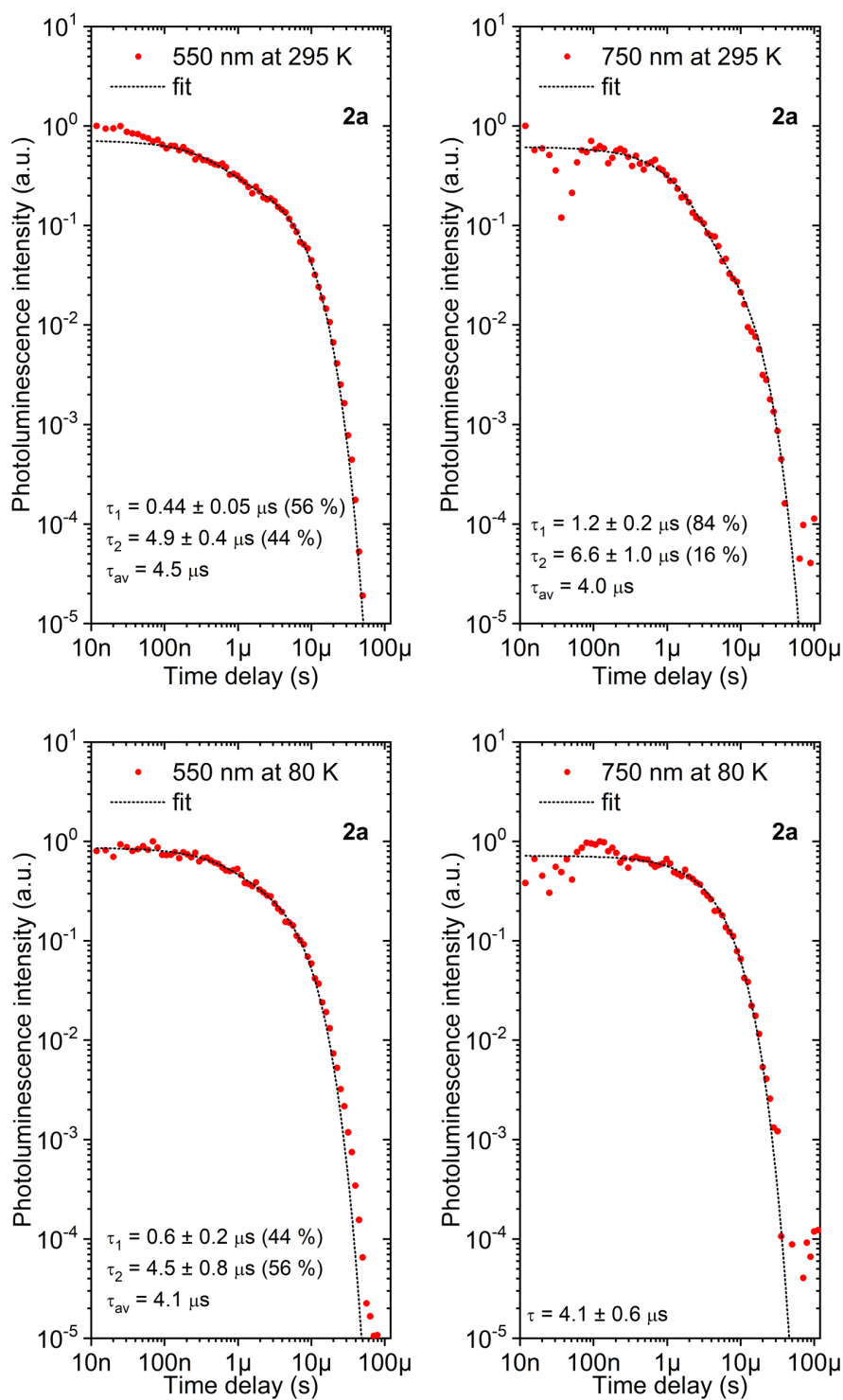
**Table S4.1** T<sub>1</sub> excited state of complexes **1a**, **2a**, and **1b-3b** calculated using the BP86/def2-SVP//CAM-B3LYP/def2-SVP/CPCM(CH<sub>2</sub>Cl<sub>2</sub>) level of theory.

Complex	Energy / eV	Transitions	Character
<b>1a</b>	1.91	HOMO→LUMO (71%) HOMO-1→LUMO (12%)	$d_{(Pt)} + p_{(Cl)} \rightarrow \pi_{(N^{\wedge}C^{\wedge}N)}^*$
<b>1b</b>	2.22	HOMO→LUMO (50%) HOMO-2→LUMO (30%)	$d_{(Pt)} + p_{(Cl)} + \pi_{(acetylide)} + \pi_{(xanthene)} \rightarrow \pi_{(N^{\wedge}C^{\wedge}N)}^*$
<b>2a</b>	1.79	HOMO→LUMO (80%) HOMO-1→LUMO (13%)	$d_{(Pt)} + p_{(Cl)} \rightarrow \pi_{(N^{\wedge}C^{\wedge}N)}^*$
<b>2b</b>	2.08	HOMO→LUMO (53%) HOMO-2→LUMO (30%)	$d_{(Pt)} + p_{(Cl)} + \pi_{(acetylide)} + \pi_{(xanthene)} \rightarrow \pi_{(N^{\wedge}C^{\wedge}N)}^*$
<b>3b</b>	1.96	HOMO→LUMO (33%) HOMO-2→LUMO (37%)	$d_{(Pt)} + p_{(Cl)} + \pi_{(acetylide)} + \pi_{(xanthene)} \rightarrow \pi_{(N^{\wedge}C^{\wedge}N)}^*$

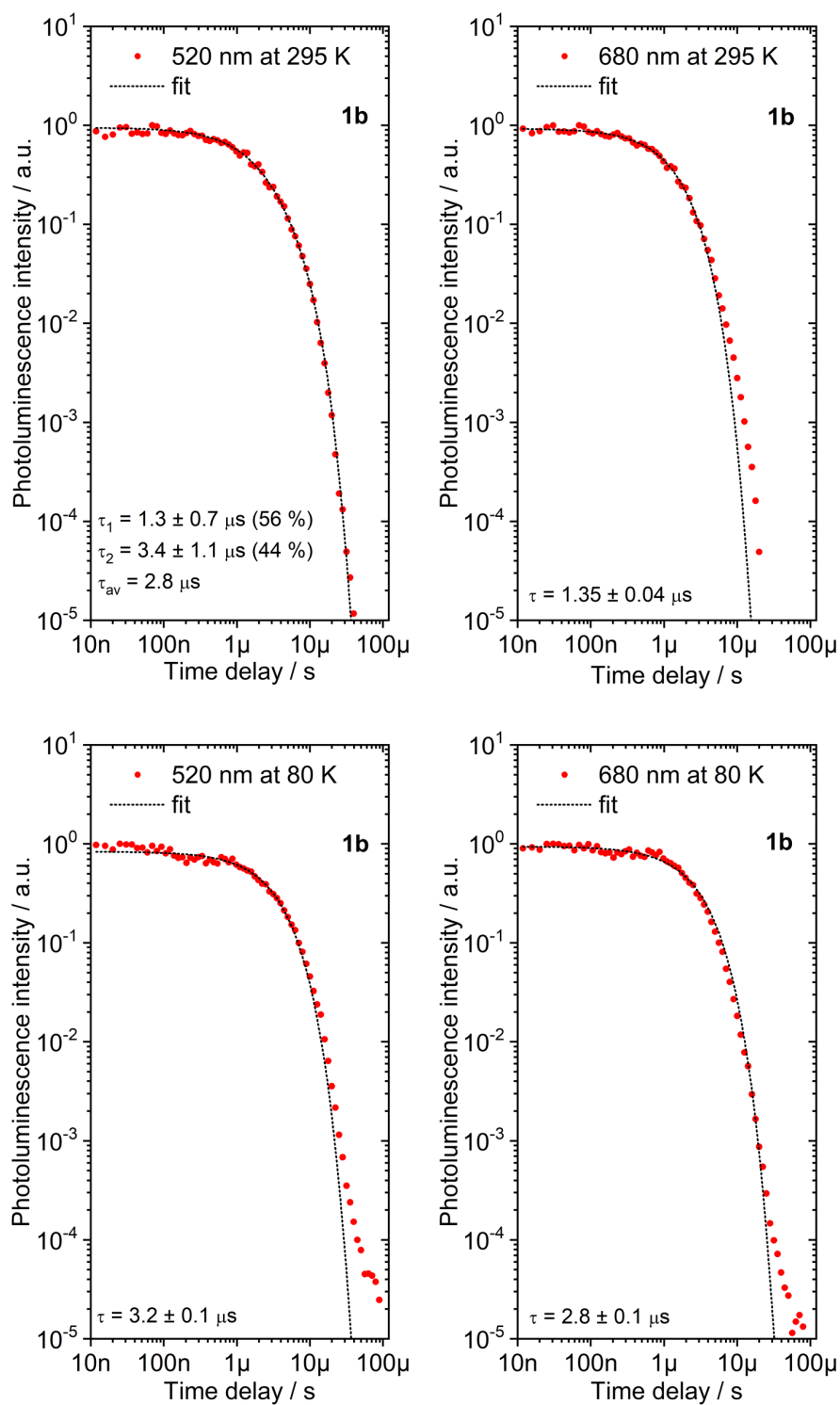
## 5. Photophysics



**Figure S5.1.** Photoluminescence decay traces of **1a** in 1% wt. film in polystyrene at 295 K and 80 K. Detection wavelengths are indicated in the legend of each figure.

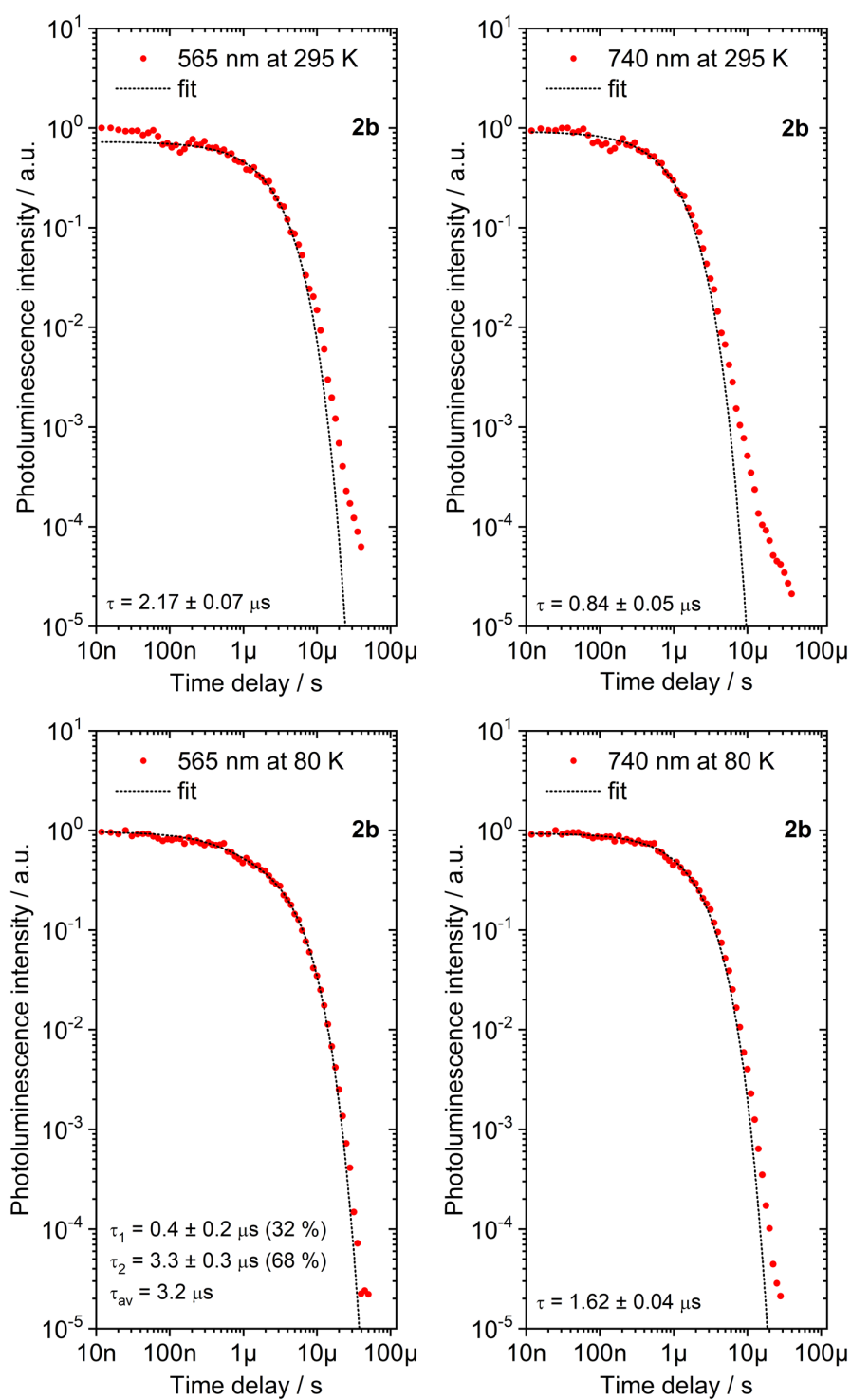


**Figure S5.2.** Photoluminescence decay traces of **2a** in 1% wt. film in polystyrene at 295 K and 80 K. Detection wavelengths are indicated in the legend of each figure.

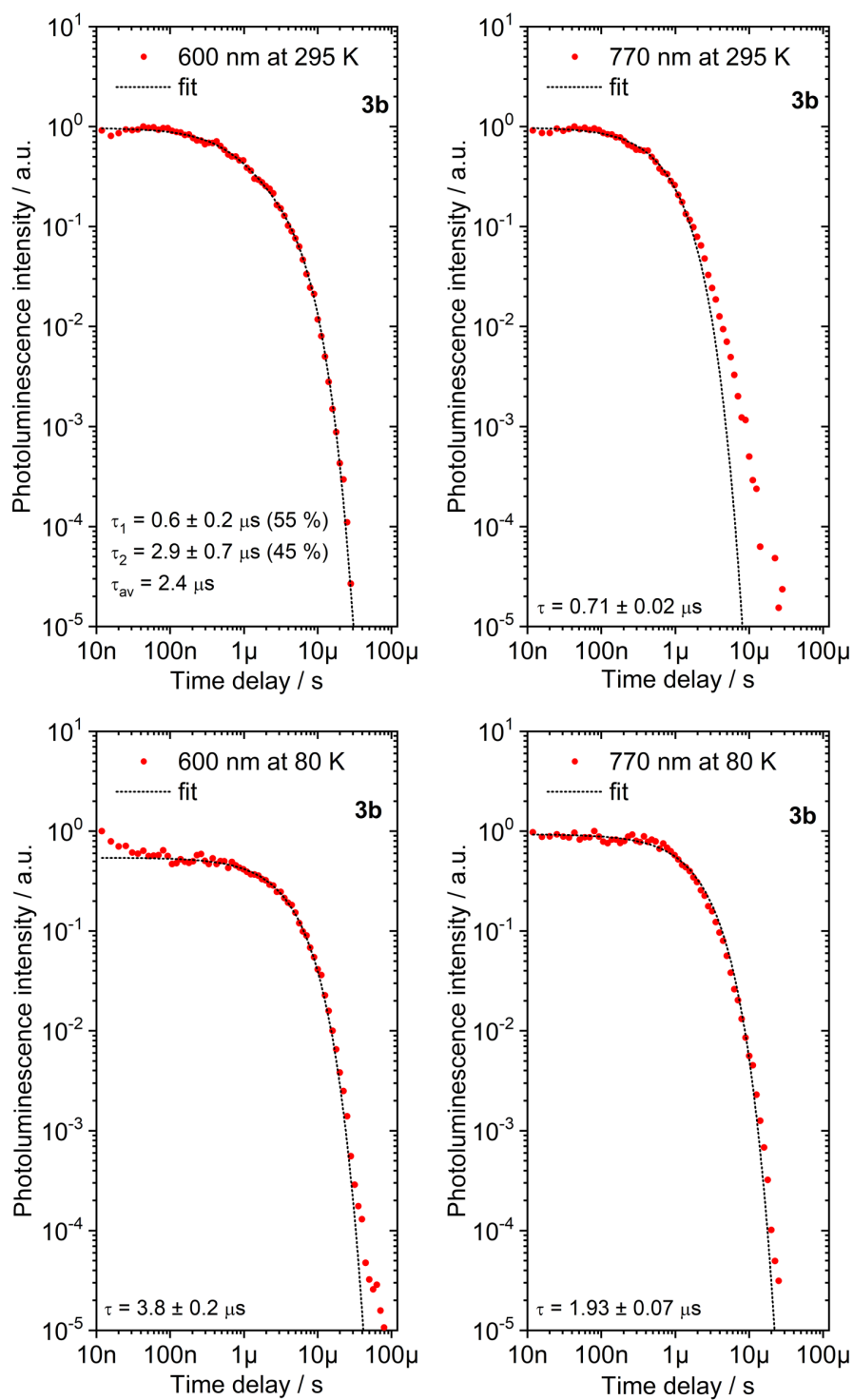


**Figure S5.3.** Photoluminescence decay traces of **1b** in 1% wt. film in polystyrene at 295 K and 80 K. Detection wavelengths are indicated in the legend of each figure.

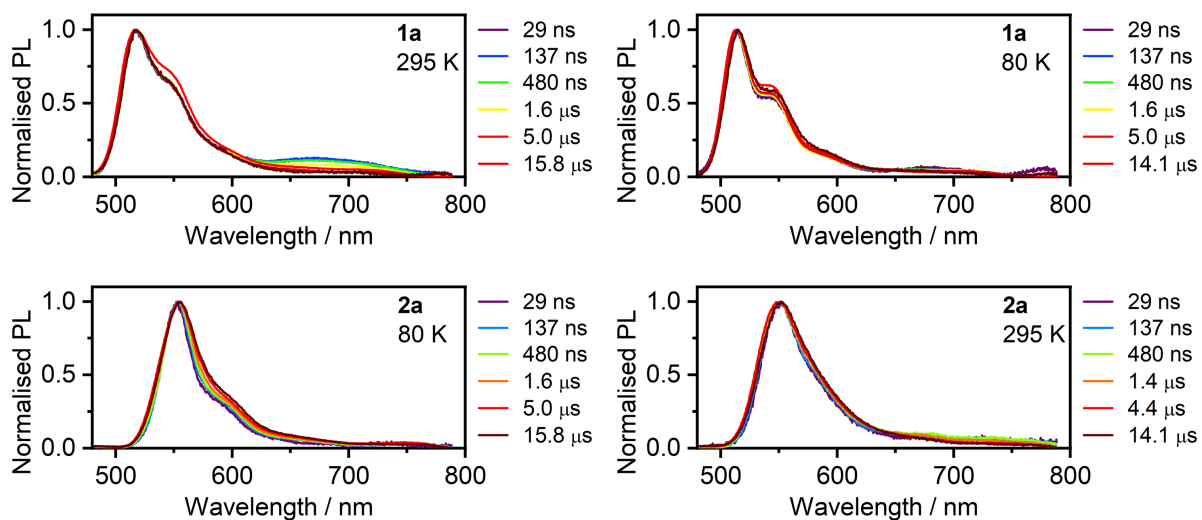




**Figure S5.4.** Photoluminescence decay traces of **2b** in 1% wt. film in polystyrene at 295 K and 80 K. Detection wavelengths are indicated in the legend of each figure.



**Figure S5.5.** Photoluminescence decay traces of **3b** in 1% wt. film in polystyrene at 295 K and 80 K. Detection wavelengths are indicated in the legend of each figure.



**Figure S5.6.** Time-resolved photoluminescence spectra of **1a** in 1% wt. film in polystyrene at 295 K and 80 K.

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