Supplementary material

Experimental Data: 2,3,4,5-tetrakis-(4-*tert*-butylphenyl)cyclopentadienone was synthesised according to a literature procedure[1]. Flash chromatography was performed using silica gel (Aldrich Chemical) as the stationary phase.

Physical measurements and instrumentation: IR spectra were recorded neat on a PerkinElmer Spectrum 100 FTIR spectrometer fitted with a Universal ATR accessory. Elemental analysis was obtained on a Carlo Erba 1006 automatic analyser. All samples were crystallised from chloroform and methanol and dried under vacuum prior to analysis.

NMR spectra of **1** and **2** were recorded on a Bruker Avance DPX 400 spectrometer operating at 400.13 MHz for ^{1}H, and 100.62 MHz for ^{13}C, or for **3** on a Bruker Avance II 600 NMR spectrometer operating at 600.13 MHz for ^{1}H, and 150.90 MHz for ^{13}C; all samples were standardised with respect to TMS. Mass spectral analysis was carried out for all samples except **2**; EI-MS were measured on a Waters corp. GCT Premier electron impact mass spectrometer and MALDI-MS on a MALDI-Q-ToF Premier mass spectrometer. Accurate MS were referenced against leucine enkephalin (555.6 gmol^{-1}), and were reported within 5 ppm. UV/Vis absorption spectra were recorded on a Shimadzu UV-2450 UV/Vis recording spectrophotometer. All electrochemical experiments were performed with a CH Instruments potentiostat model 660B. Cyclic voltammograms were measured on 1 mmol solutions of the compounds in chloroform Tetra-nbutylammonium hexafluorophosphate (Bu_4NPF_6, 0.1 M) was used as supporting electrolyte, a glassy carbon working electrode, a Pt wire counter electrode and a SCE reference electrode were used. Potentials are quoted versus the ferrocene–ferrocenium couple (0.0 V), and all potentials were referenced to internal ferrocene added at the end of each experiment. All solutions were continuously degassed for ten minutes by nitrogen bubbling, before the experiments were performed and a flow of nitrogen was maintained over the solution for the duration of the experiments. Emission and excitation spectra were obtained on a Fluorolog FL-3-11 spectrofluorimeter, in which lifetime measurements were performed with an IBH Datastation HUB 5000F. All samples were degassed under an argon atmosphere prior to the experiment being carried out. Quantum yields were measured at room temperature using quinine sulfate as quantum yield standard assuming a value of 0.54.

Synthesis of (4-*tert*-butylphenyl)(3-thienyl)acetylene (PhCCS^3): Copper (I) iodide (36 mg, 0.19 mmol), 1-*tert*-butyl-4-iodobenzene (500 mg, 0.34 mL, 1.90 mmol) and dichlorobis(triphenylphosphine) palladium (0) (112 mg, 0.10 mmol) were dissolved in degassed piperidine (20 mL). 3-ethynylthiophene (220 mg, 0.20 mL, 2.03 mmol) was added and the mixture was left stirring at room temperature for 20 hours. Dichloromethane (15 mL) was added and the solution washed first with saturated ammonium chloride and then with water. The organic phases were dried with magnesium sulfate and solvent was evaporated. The product was purified by column chromatography on silica using hexane: dichloromethane (9:1, R_f 0.7) as eluent to give the desired product as a white solid (350 mg, 1.46 mmol, 72%). **Mp:** 47-48 °C (from MeOH). $\boldsymbol{\delta_H}$ (400 MHz; $CDCl_3$; 25°C; TMS) 7.55 (1 H, dd, $^4J_{HH}$ 1.5 and 3.0 Hz, H_{Th}), 7.52 (2 H, d, $^3J_{HH}$ 8.0 Hz, H_{Ar}), 7.42 (2 H, d, $^3J_{HH}$ 8.0 Hz, H_{Ar}), 7.33 (1 H, dd, $^4J_{HH}$ 3.0 Hz and $^3J_{HH}$ 5.0 Hz, H_{Th}), 7.26 (1 H, d, $^3J_{H\text{-}H}$ 5.0 Hz, H_{Th}), 1.38 (9 H, s, CMe_3). $\boldsymbol{\delta_C}$ (100 MHz; $CDCl_3$; 25°C; TMS) 151.0 ($C_{Ar/quat}$), 130.8 (C_{Ar}), 129.2 (C_{Th}), 127.3 (C_{Th}), 124.9 (C_{Ar}), 124.8 (C_{Th}), 122.1 ($C_{Ar/quat}$), 119.7 ($C_{Th/quat}$) 88.5 (C_{acetyl}), 83.4 (C_{acetyl}), 34.4 (CMe_3), 30.7 (CH_3). **IR (neat)** υ_{max}/cm^{-1}: 2967, 2199 (C≡C), 1526, 1266, 829, 785. **EI-MS:** (Acetonitrile) *m/z* 241.1058 ([M+H]$^+$) (calc. 241.1051). **Elemental Anal:** Found: C, 79.85; H, 6.71%. Calc. for $C_{16}H_{16}S$: C, 79.95; H, 6.81%.

Synthesis of 1: (4-*tert*-butylphenyl)(3-thienyl)acetylene (0.32 mmol), 2,3,4,5-tetrakis-(4-*tert*-butylphenyl)cyclopentadienone (150 mg, 0.25 mmol) and benzophenone (0.5 g) were heated for 90 minutes at 300°C while attached to an air condenser, giving a brown mixture. After cooling to room temperature, this was purified by flash chromatography (SiO_2, hexane: diethyl ether, 9:1, R_f 0.6) to give the product as a grey solid which was recrystallised from a mixture of chloroform and methanol (2 mL of each) (182 mg, 0.22 mmol, 87%). **Mp:** 307-308 °C (from MeOH). $\boldsymbol{\delta_H}$ (400 MHz; $CDCl_3$; 25°C; TMS) 6.90 (4 H, d, $^3J_{HH}$ 8.5 Hz, H_{Ar}), 6.83 (2 H, d, $^3J_{HH}$ 8.5 Hz, 2H, H_{Ar}), 6.82 (4 H, d, $^3J_{HH}$ 8.5 Hz, H_{Ar}), 6.77 (5 H, m, H_{Ar} and H_{Th}), 6.69 (2 H, d, $^3J_{HH}$ 8.5 Hz, H_{Ar}), 6.68 (4 H, d, $^3J_{HH}$ 8.5 Hz, H_{Ar}), 6.50 (1 H, dd, $^4J_{HH}$ 1.0 and 3.0 Hz, H_{Th}), 6.47 (1 H, dd, $^4J_{HH}$ 1.0 and $^3J_{HH}$ 5.0 Hz, H_{Th}), 1.20 (18 H, s, 2*CMe_3), 1.16 (27 H, m, 3*CMe_3). $\boldsymbol{\delta_C}$ (100 MHz; $CDCl_3$; 25°C; TMS) 147.3 (C_{quat}), 147.0 (C_{quat}), 146.9 (C_{quat}), 140.4 (C_{quat}), 140.2 (C_{quat}), 140.2 (C_{quat}), 140.1 (C_{quat}), 137.5 (C_{quat}), 137.4 (C_{quat}), 134.5 (C_{quat}), 130.6 ($C_{Th/quat}$ and 2*C_{Ar}), 130.3 (C_{Th}), 130.2 (C_{Ar}), 124.2 (C_{Th}), 122.9 (C_{Ar}), 122.6 (C_{Ar}), 122.5 (C_{Ar}), 121.6 (C_{Th}), 33.7 (*C*Me_3), 33.6 (2**C*Me_3), 30.8 (2**C*H_3), 30.7 (CH_3). **IR (neat)** υ_{max}/cm^{-1}: 2960, 1509, 1460, 1361, 1269, 830, 764. **MALDI-MS** (Chloroform) *m/z* 820.5008 ([M]$^+$) (calc. 820.5042). **Elemental Anal:** Found: C, 87.54; H, 8.23%. Calc. for $C_{60}H_{68}S$: C, 87.75; H, 8.35%.

Synthesis of 2 and 3: 1 (0.065 mmol) was dissolved in dry dichloromethane (20 mL) and an excess of $FeCl_3$ (0.189 g, 1.12 mmol, 20 eq.) in nitromethane (3 mL) was added dropwise under bubbling nitrogen. The mixture was left stirring for 5 hours giving a brown solution. This was quenched with methanol (30 mL), poured into water, extracted into chloroform, dried over $MgSO_4$ and solvent evaporated.

(2) Purified by silica column with dichloromethane: hexane (1:1, R_f 0.7) as eluent. (14.2 mg, 0.018 mmol, 28%). **Mp** > 320 °C (from MeOH). $\boldsymbol{\delta_H}$ (400 MHz; $CDCl_3$; 25°C; TMS) 9.31 (1 H, s, H_{10}), 9.26 (3 H, m, H_7, H_8 and H_{11}), 9.23 (1 H, s, H_6), 9.20 (1 H, s, H_5), 9.17 (1 H, s, H_4), 9.10 (1 H, s, H_3), 9.04 (1 H, s, H_2), 8.95 (1 H, s, H_9), 8.22 (1 H, s, H_{11}), 1.89 (9 H, s, CMe_3), 1.86 (18 H, s, 2*CMe_3), 1.76 (9 H, s, CMe_3), 1.72 (9 H, s, CMe_3). $\boldsymbol{\delta_C}$ (150.9 MHz; $CDCl_3$; 25°C; TMS) 149.2 (C_{quat}), 148.9 (C_{quat}), 148.6 (2*C_{quat}), 148.5 (C_{quat}), 148.4 (C_{quat}), 132.1 (C_{quat}), 130.8 (C_{quat}), 130.3 (C_{quat}), 130.2 (3*C_{quat}), 130.1 (4*C_{quat}), 127.9 (C_{quat}), 127.4 (C_{quat}), 127.2 (C_{quat}), 125.4 (C_{quat}), 124.4 (C_{quat}), 123.8 (C_{quat}), 123.7 (C_{quat}), 123.2 (C_{quat}), 122.4 (C_{quat}), 121.4 (C_{Ar}), 120.0 (C_{quat}), 119.4 (C_{quat}), 119.0 (2*C_{Ar}), 118.9 (2*C_{Ar}), 118.8 (C_{Ar}), 118.7 (3*C_{Ar}), 118.3 (C_{Th}), 118.2 (C_{quat}), 118.1 (C_{quat}), 117.7 (C_{Ar}), 35.6 (3*CMe_3), 35.4 (2*CMe_3), 32.2 (2*CH_3), 32.1 (CH_3), 32.0 (CH_3), 31.9 (CH_3). **IR (neat)** υ_{max}/cm^{-1}: 2954, 1604, 1574, 1461, 1362, 1260, 869, 763, 750. **Elemental Anal:** Found: C, 83.88; H, 6.51%. Calc. for $C_{50}H_{56}S.0.5CHCl_3$: C, 83.56; H, 6.55%.

(3) Purified by silica column with dichloromethane: hexane (1:1, R_f 0.4) as eluent. (14.9 mg, 0.009 mmol, 28%). **Mp** > 320 °C (from MeOH). $\boldsymbol{\delta_H}$ (600 MHz; $CDCl_3$; 25°C; TMS) 9.43 (2 H, s, H_{Ar}), 9.41 (2 H, s, H_{Ar}), 9.38 (4 H, s, 2*H_{Ar}), 9.35 (2 H, s, H_{Ar}), 9.31 (2 H, s, H_{Ar}), 9.12 (2 H, s, H_{Ar}), 8.87 (2 H, s, H_{Ar}), 8.86 (2 H, s, H_{Ar}), 8.75 (2 H, s, H_{Ar}), 1.89 (36 H, m, 2*CMe_3), 1.80 (36 H, m, 2*CMe_3), 0.58 (18 H, s, CMe_3). $\boldsymbol{\delta_C}$ (150.9 MHz; $CDCl_3$; 25°C; TMS) 149.7 (C_{quat}), 149.5 (C_{quat}), 149.0 (C_{quat}), 148.8 (C_{quat}), 148.7 (C_{quat}), 135.4 (C_{quat}), 134.1 (C_{quat}), 132.0 (C_{quat}), 131.2 (C_{quat}), 130.5 (3*C_{quat}), 130.4 (C_{quat}), 130.3 (3*C_{quat}), 130.2 (C_{quat}), 129.1 (C_{quat}), 128.9 (C_{quat}), 128.2 (C_{quat}), 128.1 (C_{quat}), 127.9 (C_{quat}), 125.2 (C_{quat}), 124.9 (C_{quat}), 124.1 (2*C_{quat}), 123.5 (C_{quat}) , 123.2 (C_{quat}), 122.2 (C_{Ar}), 123.5 (C_{quat}), 119.9 (C_{quat}), 119.5 (C_{Ar}), 119.2 (C_{Ar}), 119.1 (C_{Ar}), 119.0 (C_{Ar}), 118.9 (C_{Ar}), 118.7 (C_{Ar}), 118.6 (C_{Ar}), 118.5 (C_{Ar}), 118.2 (C_{Ar}), 35.7 (2**C*Me_3), 35.5 (*C*Me_3), 35.5 (*C*Me_3), 34.6 (*C*H_3), 32.0 (2**C*H_3), 31.9 (CH_3), 30.4 (*C*H_3). **IR (neat)** υ_{max}/cm^{-1}: 2953, 1604, 1575, 1476, 1471, 1362, 1258, 866, 761. **MALDI-MS** (Acetonitrile) *m/z* 1614.8081 ([M]$^+$) (calc.1614.8049). **Elemental Anal:** Found: C, 78.75; H, 6.36%. Calc. for $C_{120}H_{110}S_2.2.0CHCl_3$: C, 78.75; H, 6.08%.

[1] S. Sadhukhan, C. Viala, A. Gourdon, *Synthesis-Stuttgart* **2003**, 1521-1525.

UV/Visible and Luminescence data

Table 1: Absorption data for complexes **1-3** ($CHCl_3$, 10^{-5}M).

	λ [nm] (10^3 ε [$mol^{-1}L\ cm^{-1}$])
1	257 (4.1), 277*sh* (2.9).
2	241 (9.0), 340*sh* (4.7), 358 (8.0), 369 (8.4), 408 (2.1), 432 (2.0)
3	243 (16.1), 358 (14.0), 368 (14.7), 409*sh* (5.4), 433*sh* (3.6), 464*sh* (2.2) (tail till 550)

Table 2: Luminescence quantum yield values for **2-3** ($CHCl_3$).

	in air	**in argon**
2	0.024	0.030
3	0.011	0.018

Table 3. Luminescence data for compounds **1-3**.

		T[K]	λexc [nm]	λem [nm]	τ [ns] (all at 298K)
1	solid	298	371 *br* (λ_{em} 465)	460 *br* (λ_{exc} 360)	59.4(12%), 529.6(88%), (λ_{exc}370-λ_{em}460)
		77	325 (λ_{em} 360)	360, 485$_{max}$, 519 (λ_{exc} 320)	
			323, 375*br* (λ_{em} 495)	480 *br* (λ_{exc} 375)	
	$CHCl_3$, 10^{-3} M	298	325 (λ_{em} 375)	375 (λ_{exc} 320)	2.7(28%), 10.2(72%) (λ_{exc}340-λ_{em}375)
			325$_{max}$, 364 (λ_{em} 445)	375*sh*, 420*sh*, 445$_{max}$, 475*sh* (λ_{exc} 360)	4.3(38%), 14.2(62%) (λ_{exc}370-λ_{em}450)
		77	290 (λ_{em} 345)	346, 442*sh*, 472$_{max}$ (λ_{exc} 285)	
			290$_{max}$, 311, 341, 365 (λ_{em} 480)	430sh, 448$_{max}$, 482 (λ_{exc} 485)	
2	solid	298	307 (λ_{em} 370)	368, 390 *sh* (λ_{exc} 305)	29.4(54%), 49.0(46%) (λ_{exc}295-λ_{em}370)
			314$_{max}$, 365, 385, 402 (λ_{em} 530)	509$_{max}$, 533 (λ_{exc} 370)	388.5(22%), 2285.1(12%) (λ_{exc}370-λ_{em}510)
		77	308 (λ_{em} 370)	373$_{max}$, 485*br* (λ_{exc} 310)	
			308, 366, 399*sh* (λ_{em} 480)	409, 435, 491$_{max}$, 531*sh* (λ_{exc} 365)	
	$CHCl_3$, 10^{-3} M	298	290*sh*, 313$_{max}$, 351, 370, 385, 404, 430, 456, 475, 491 (λ_{em} 540)	454, 471, 475, 495, 505$_{max}$, 530, 537, 575*sh* (λ_{exc} 367)	9.7(95%), 28.8(5%) (λ_{exc}370-λ_{em}476) 9.4(84%), 24.0(16%) (λ_{exc}370-λ_{em}504) 11.7(32%), 373.7(68%) (λ_{exc}370-λ_{em}580)
		77	290*sh*, 320, 355, 392, 408, 433$_{max}$ (λ_{em} 475)	479sh, 492, 510$_{max}$, 535*sh*, 575, 623*sh*, 634, 697 (λ_{exc} 394)	
3	solid	298	307 (λ_{em} 365)	366 (λ_{exc} 305)	16.2(10%), 38.7(90%) (λ_{ex}295-λ_{em}370)
			325$_{max}$, 365 (λ_{em} 540)	543, 573*sh* (λ_{exc} 365)	404.7(25%), 2503.4(75%) (λ_{exc}370-λ_{em}540)
		77	307 (λ_{em} 365)	366, 380*sh*, 477$_{min}$ (λ_{exc} 305)	
			308$_{max}$, 370, 397 (λ_{em} 480)	412, 435, 478$_{max}$, 528 (λ_{exc} 370)	
	$CHCl_3$, 10^{-3} M	298	527 (λ_{em} 580)	580 (λ_{exc} 525)	3.5(37%), 15.7(63%) (λ_{exc}460-λ_{em}580)
		77	365, 397, 410, 452*sh*, 440, 555, 595*sh* (λ_{em} 640)	567, 600*sh*, 637 (λ_{exc} 430)	
				624, 660*sh* (λ_{exc} 590)	
	$CHCl_3$, 10^{-5} M	298	290*sh*, 360$_{max}$, 386, 410, 430, 463 (λ_{em} 495)	472, 485, 494$_{max}$, 504, 528, 565 (λ_{exc} 360)	10.9(23%), 24.8(77%) (λ_{exc}370-λ_{em}485)
		77	330, 366$_{max}$, 428, 470 (λ_{em} 529)	470, 503*sh*, 529, 540*sh*, 569$_{max}$, 623, 647 (λ_{exc} 360)	

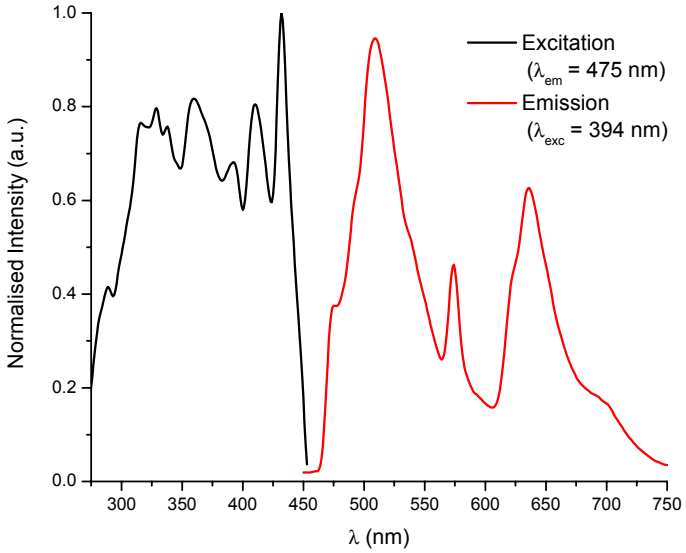

Figure S1: Luminescence spectra of **2** at 77K (chloroform 10^{-3} M)