

**Unsymmetrical Triphenylamine–Cyanostilbene Donor–Acceptor Fluorophores:  $\pi$ -Spacer-Controlled Charge Transfer and Aggregation-Dependent Luminescence**

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## 1. Materials and measurements

The starting material for the synthetic scheme triphenylamine and chemicals including bithiophene, N-bromosuccinimide(NBS),dichlorobis(triphenylphosphine)palladium(II), tetrakis(triphenylphosphine)palladium(0),benzylcyanide,potassium carbonate( $K_2CO_3$ ),Phosphoryl trichloride ( $POCl_3$ ), sodium hydroxide(NaOH), dimethylformamide(DMF), chloroform ( $CHCl_3$ ), tetrahydrofuran (THF) methanol (MeOH), Acetic acid ( $CH_3COOH$ ) and Dimethyl formamide(DMF) were purchased from a commercial supplier and used as received. DMF and Toluene was dried by storing it over 4 Å molecular sieves that had been activated by heating in a preheated 150 °C oven. All chromatographic purifications were done using silica gel (100-200 mesh). The  $^1H$  and  $^{13}C$  NMR spectra of the synthesized compounds were recorded on a JEOL JNM-ECZ-500R/M1 (500 MHz) NMR instrument using  $CDCl_3$  as the solvent, and tetramethylsilane (TMS) as an internal standard. High-resolution mass spectrometry (HRMS) data were acquired on a Waters Synapt XS spectrometer in positive ion mode, with a fragmentor voltage of 3.01 kV, cone voltage of 35 V, source offset of 4.0 V, source temperature of 120 °C, and cone gas flow rate of 50 L/h, and the ion values are reported as m/z. The UV–vis absorption spectra was measured using a LAMBDA 365 UV/Vis Spectrophotometer with keeping slit width 2. Fluorescent measurements were carried out on perkinelmer LS-55 fluorescence spectrometer. The solid-state measurements were measured on Horiba fluorescence spectrophotometer.

### Synthesis of **4-(phenyl(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)amino)benzaldehyde**

To a flame-dried Schlenk flask equipped with a magnetic stirring bar under a nitrogen atmosphere were added 4-((4-bromophenyl)(phenyl)amino)benzaldehyde (2.00 g, 5.68 mmol), bis(pinacolato)diboron (2.16 g, 8.52 mmol), potassium acetate (1.67 g, 17.03 mmol), triphenylphosphine (0.0596 g, 0.22 mmol), and  $Pd(PPh_3)_2Cl_2$  (0.16 mmol). Degassed toluene (20 mL) was added via syringe, and the reaction mixture was stirred at 110 °C for 24 h under nitrogen. The progress of the reaction was monitored by TLC. After completion, the reaction mixture was cooled to room temperature, and the solvent was removed under reduced pressure. The residue was extracted with dichloromethane, washed thoroughly with water, dried over anhydrous  $Na_2SO_4$ , and filtered. Concentration of the organic layer afforded the crude product, which was purified by silica gel column chromatography using hexane/ethyl acetate as the eluent. Evaporation of the solvent followed by drying under high vacuum afforded the desired

product as a yellow semisolid (1.37 g, 60.3% yield).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  9.82 (s, 1H), 7.78 – 7.74 (m, 2 H), 7.70 – 7.67 (m, 2 H), 7.33 (d,  $J$  = 7.5 Hz, 2 H), 7.26 (s, 1 H), 7.19 – 7.12 (m, 6 H), 7.06 (d,  $J$  = 8.7 Hz, 2 H), 1.34 (s, 12 H).

#### Synthesis of compound 1

An oven-dried Schlenk round-bottom flask equipped with a magnetic stirring bar was charged with 4-(phenyl(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)amino)benzaldehyde (0.55 g, 1.56 mmol), which was dissolved in tetrahydrofuran (THF, 40 mL). To this solution were added an aqueous solution of potassium carbonate ( $\text{K}_2\text{CO}_3$ , 2M, 5 mL) and *p*-bromobenzaldehyde (0.23 g, 1.25 mmol). The reaction mixture was degassed by bubbling nitrogen gas through the solution for 30 min. Subsequently, tetrakis(triphenylphosphine)palladium(0) [ $\text{Pd}(\text{PPh}_3)_4$ ] (0.016 g, 0.014 mmol) was added under a nitrogen atmosphere. The resulting mixture was heated under reflux with continuous stirring for 24 h. The progress of the reaction was monitored by thin-layer chromatography (TLC). Upon completion, the reaction mixture was allowed to cool to room temperature, and the solvent was removed under reduced pressure using a rotary evaporator. The crude residue was extracted with dichloromethane (DCM), and the organic layer was washed thoroughly with distilled water. The organic phase was dried over anhydrous sodium sulfate, filtered, and concentrated under reduced pressure to afford the crude product. Purification was carried out by silica gel column chromatography using hexane/ethyl acetate (85:15, v/v) as the eluent. The desired product was obtained as a white solid (**1**) (0.34 g, yield: 71 %).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  10.05 (s, 1H), 9.84 (s, 1H), 7.94 (d,  $J$  = 8 Hz, 2H), 7.76 (m, 5H), 7.61 (d,  $J$  = 8 Hz, 2H), 7.39 (m, 2H), 7.24 (m, 5H), 7.13 (d,  $J$  = 8 Hz, 3H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  191.9, 190.6, 153.0, 146.8, 146.2, 146.1, 135.7, 135.2, 131.4, 130.5, 130.0, 129.9, 128.6, 127.3, 126.6, 125.9, 125.6, 120.4.

#### Synthesis of compound 2

Product **2** was synthesized following the procedure described for procedure **1**, using the quantities specified below. 4-(phenyl(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)amino)benzaldehyde (0.55 g, 1.39 mmol), 5-bromothiophene-2-carbaldehyde (0.230 g, 1.2081 Mmol), THF (20 ml), potassium carbonate (2N, 7 ml) and [ $\text{Pd}(\text{PPh}_3)_4$ ] (0.016 g, 0.014 mmol) (0.36 g, yield: 77 %).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  9.88 (s, 1H), 9.85 (s, 1H), 7.73 (m, 3H), 7.61(m, 2H), 7.38 (m, 3H), 7.23 (dd,  $J$  = 4.8, 3.8 Hz, 1H), 7.18 (m, 4 H), 7.13 (m, 2H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  190.6, 182.8, 153.7, 152.7, 147.5, 145.9, 142.2, 137.7, 131.4, 130.2, 130.1, 127.7, 126.6, 125.4, 123.7, 120.9.

### Synthesis of **TPA-Ph-(CN)<sub>2</sub>**

A round-bottom flask equipped with a magnetic stirring bar was charged with compound **1** (0.2 g, 0.53 mmol) and methanol (50 mL). The mixture was stirred until a homogeneous suspension was obtained, after which sodium hydroxide (0.21 g, 5.31) was added. Upon dissolution of the reactants, benzyl cyanide (0.37 g, 3.18 mmol) was added dropwise, and the reaction mixture was stirred at room temperature. Initially, the reaction mixture appeared yellow. The reaction was continued until completion, as monitored by thin-layer chromatography (TLC). The resulting solid product was isolated by vacuum filtration using Whatman filter paper and washed several times with methanol to remove impurities. After washing, the product was obtained as a yellow solid, which was dried under vacuum to afford the desired compound in 0.36 g yield. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.03 (d, *J* = 7.5 Hz, 2H), 7.98 (d, *J* = 7.5 Hz, 2H), 7.71 (m, 6H), 7.62 (d, *J* = 7.5 Hz, 3H), 7.48 (m, 6H), 7.37 (m, 4H), 7.25 (m, 9H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 149.6, 146.8, 146.5, 142.4, 141.8, 141.7, 135.2, 135.0, 134.6, 132.5, 130.8, 130.0, 129.8, 129.2, 129.1, 128.2, 127.1, 126.1, 125.8, 125.3, 124.8, 121.8, 118.8, 118.3, 111.2, 108.3.

### Synthesis of **TPA-Th-(CN)<sub>2</sub>**

Product **TPA-Th-(CN)<sub>2</sub>** was synthesized following the procedure described for procedure **TPA-Ph-(CN)<sub>2</sub>**, using the quantities specified below. 5-(4-((4-formylphenyl)(phenyl)amino)phenyl)thiophene-2-carbaldehyde (0.17 g, 0.44 mmol), benzyl cyanide (0.31 g, 2.66 mmol), methanol (50 mL), NaOH (0.18 g, 4.42 mmol). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.82 (d, *J* = 8.1 Hz, 2H), 7.62 (dd, *J* = 20.4, 11.9 Hz, 7H), 7.36 (m, 9H), 7.19 (m, 6H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 149.3, 148.7, 147.2, 146.3, 141.6, 136.7, 135.0, 134.2, 134.1, 130.8, 129.8, 129.2, 129.1, 127.3, 126.1, 125.8, 125.7, 125.0, 124.9, 123.2, 122.1, 108.5, 107.2.

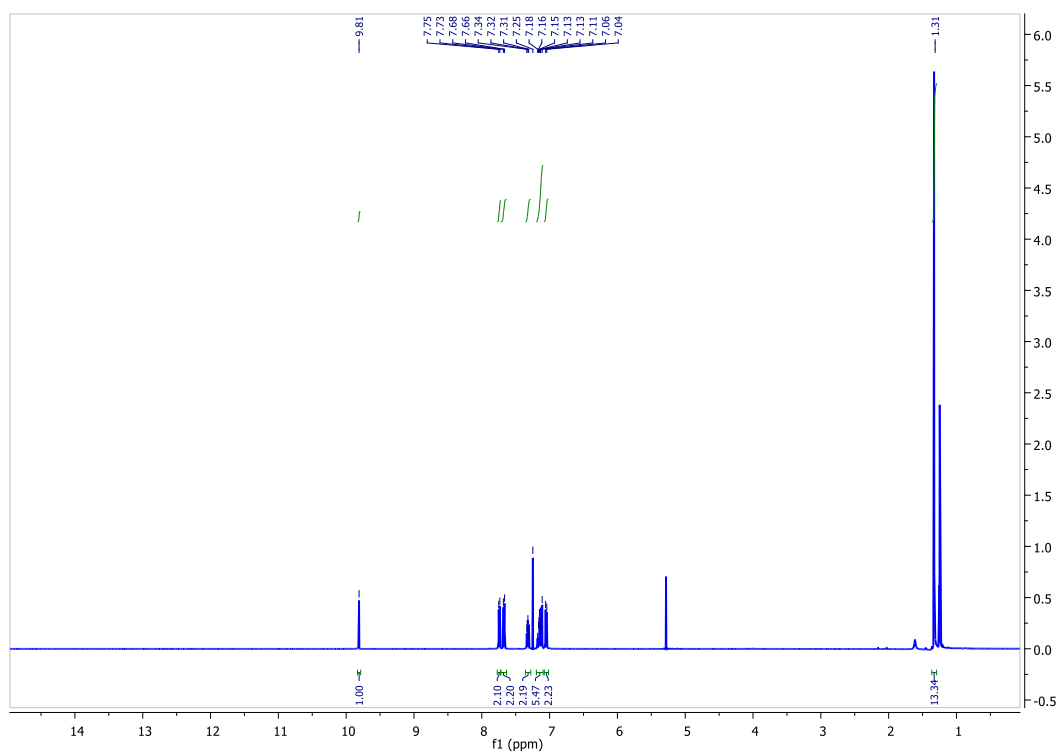


**Figure S1.** <sup>1</sup>H NMR of 4-(phenyl(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)amino)benzaldehyde (CDCl<sub>3</sub>, 500 MHz, RT)

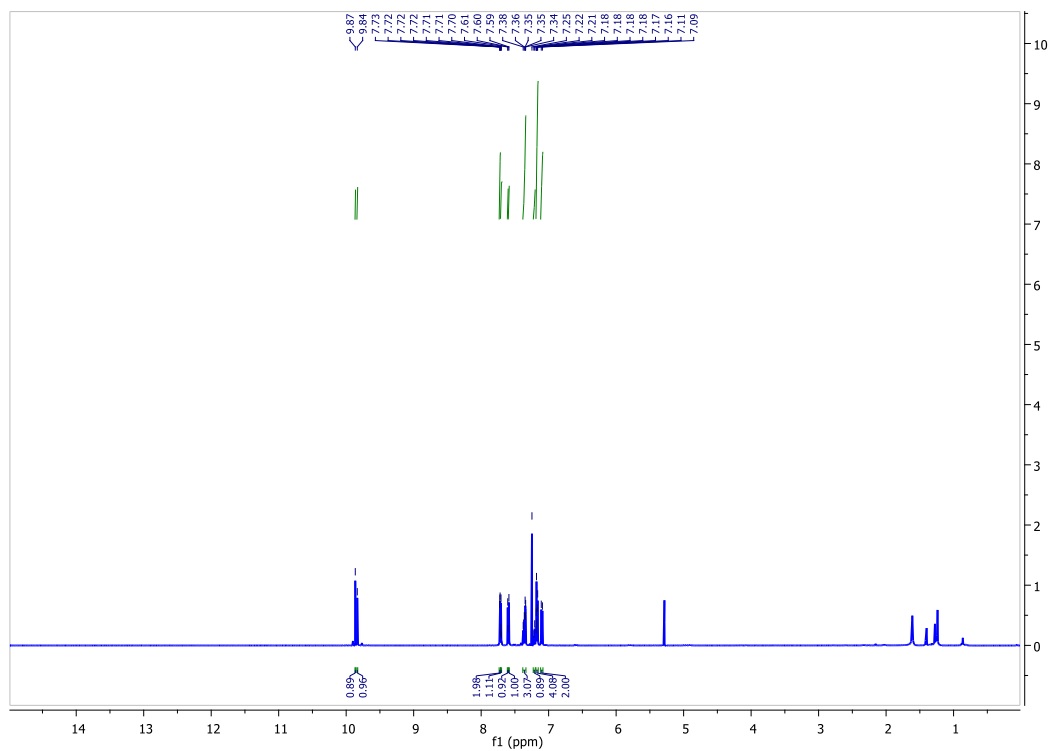


**Figure S2.** <sup>1</sup>H NMR of **1** (CDCl<sub>3</sub>, 500 MHz, RT)

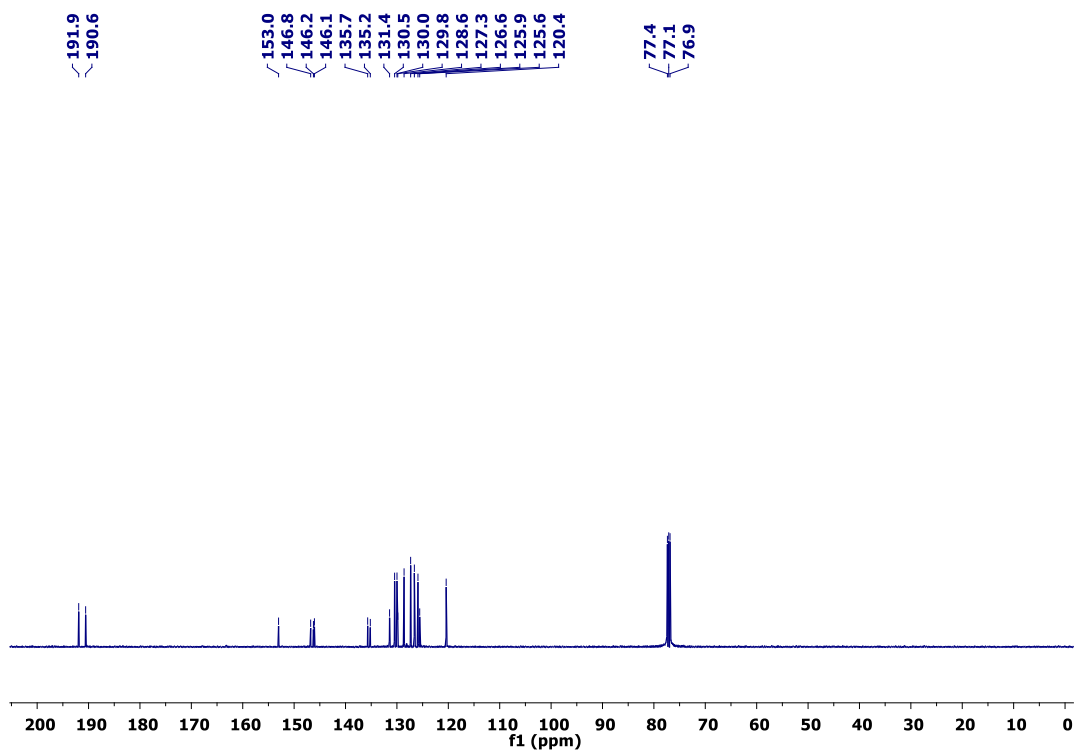


**Figure S3.** <sup>13</sup>C NMR of **1** (CDCl<sub>3</sub>, 500 MHz, RT)

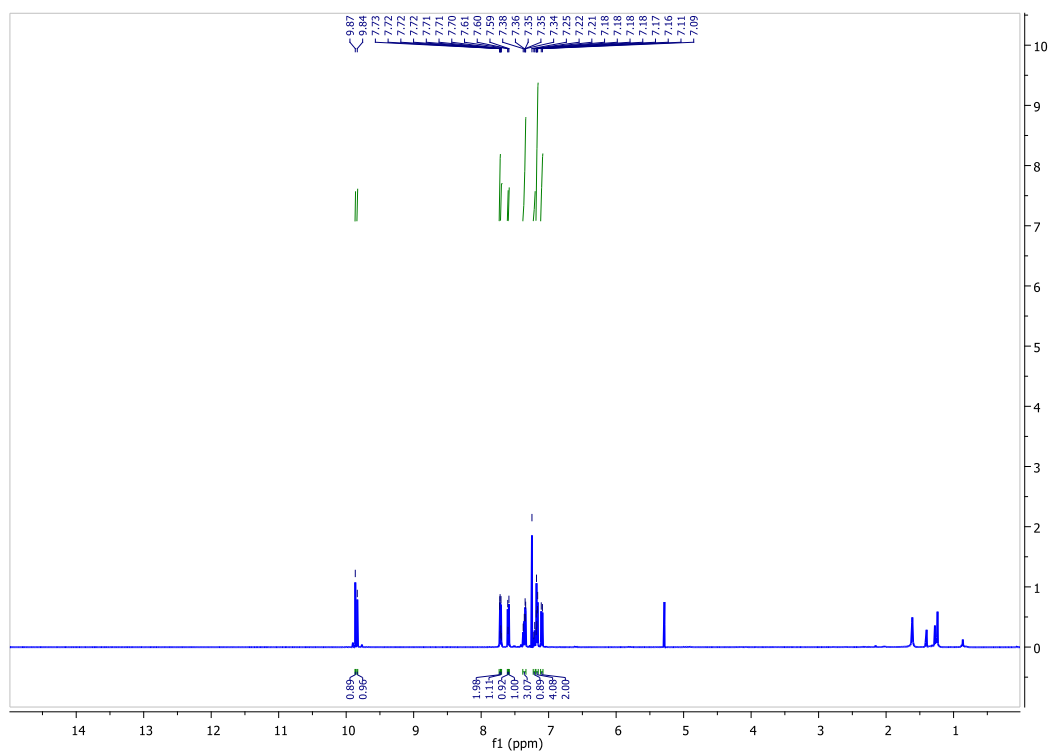


**Figure S4.** <sup>1</sup>H NMR of **2** (CDCl<sub>3</sub>, 500 MHz, RT)

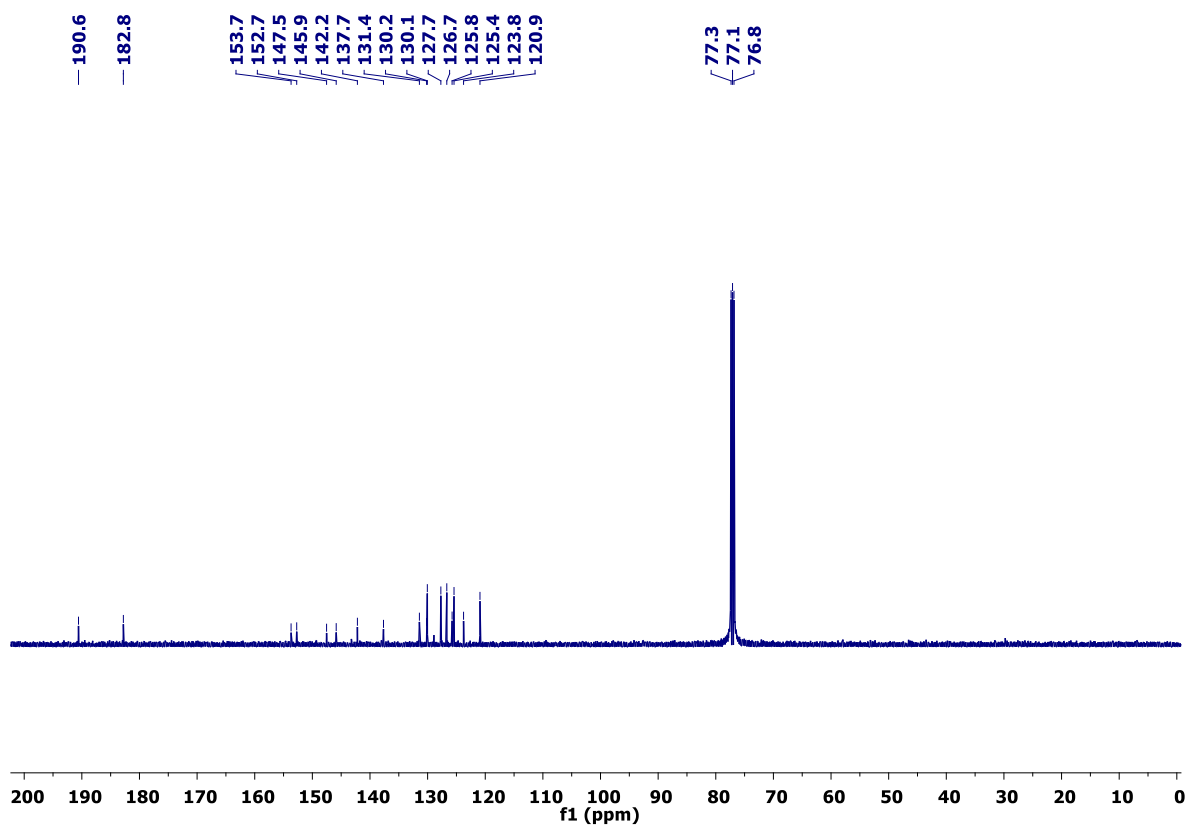


**Figure S5.** <sup>13</sup>C NMR of 2 (CDCl<sub>3</sub>, 500 MHz, RT)

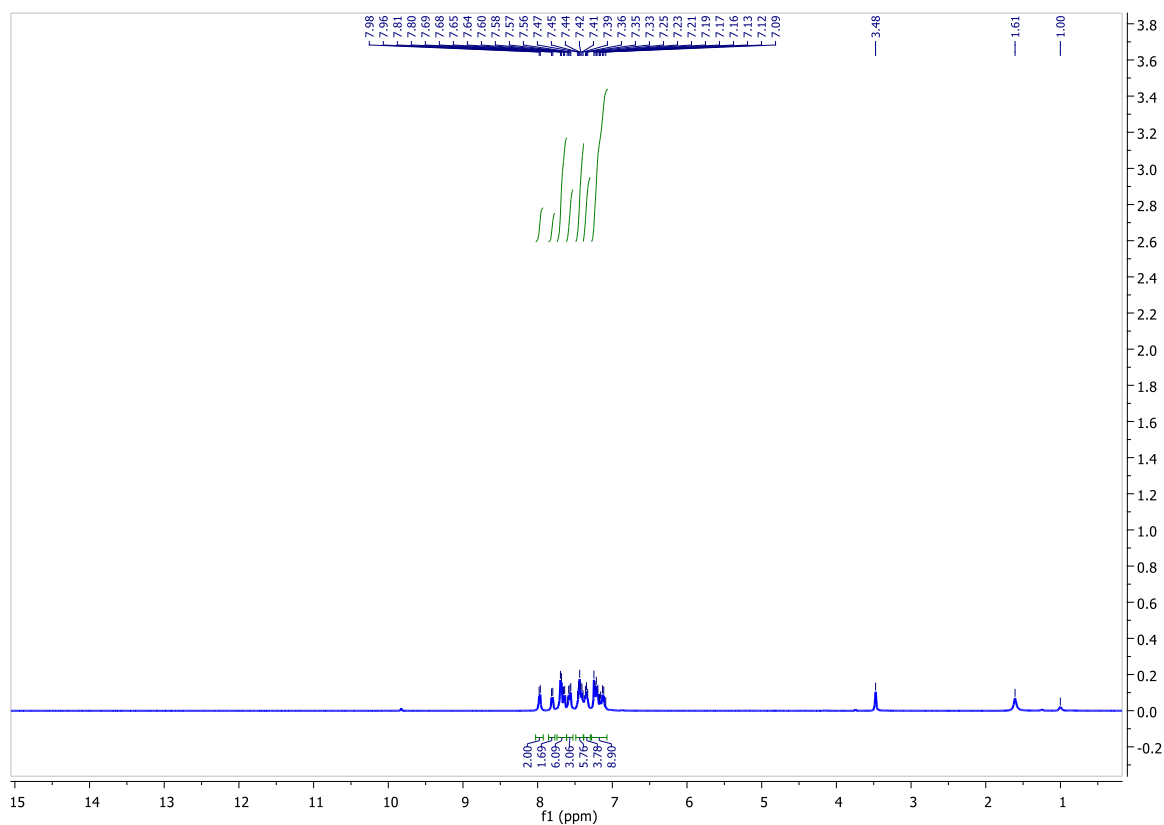


**Figure S6.** <sup>1</sup>H NMR of TPA-Ph-(CN)<sub>2</sub> (CDCl<sub>3</sub>, 500 MHz, RT)

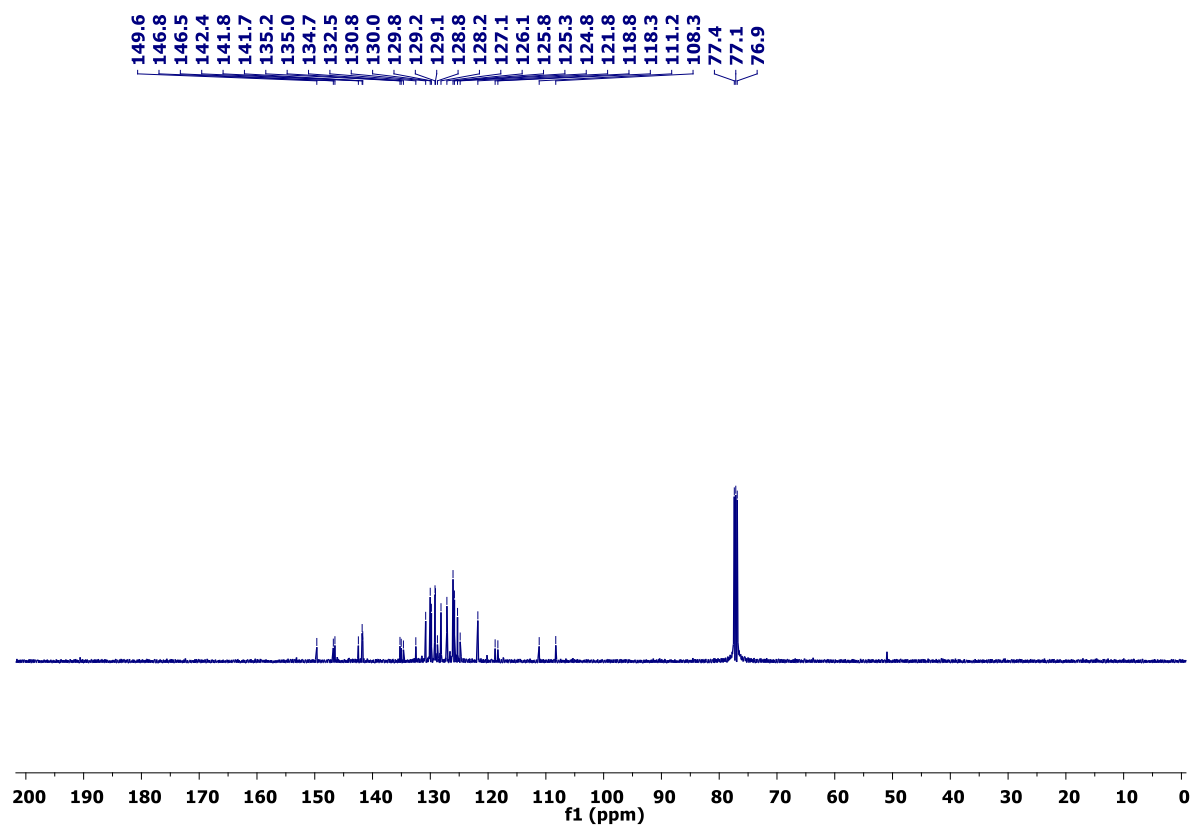


**Figure S7.**  $^{13}\text{C}$  NMR of TPA-Ph-(CN) $_2$  ( $\text{CDCl}_3$ , 500 MHz, RT)

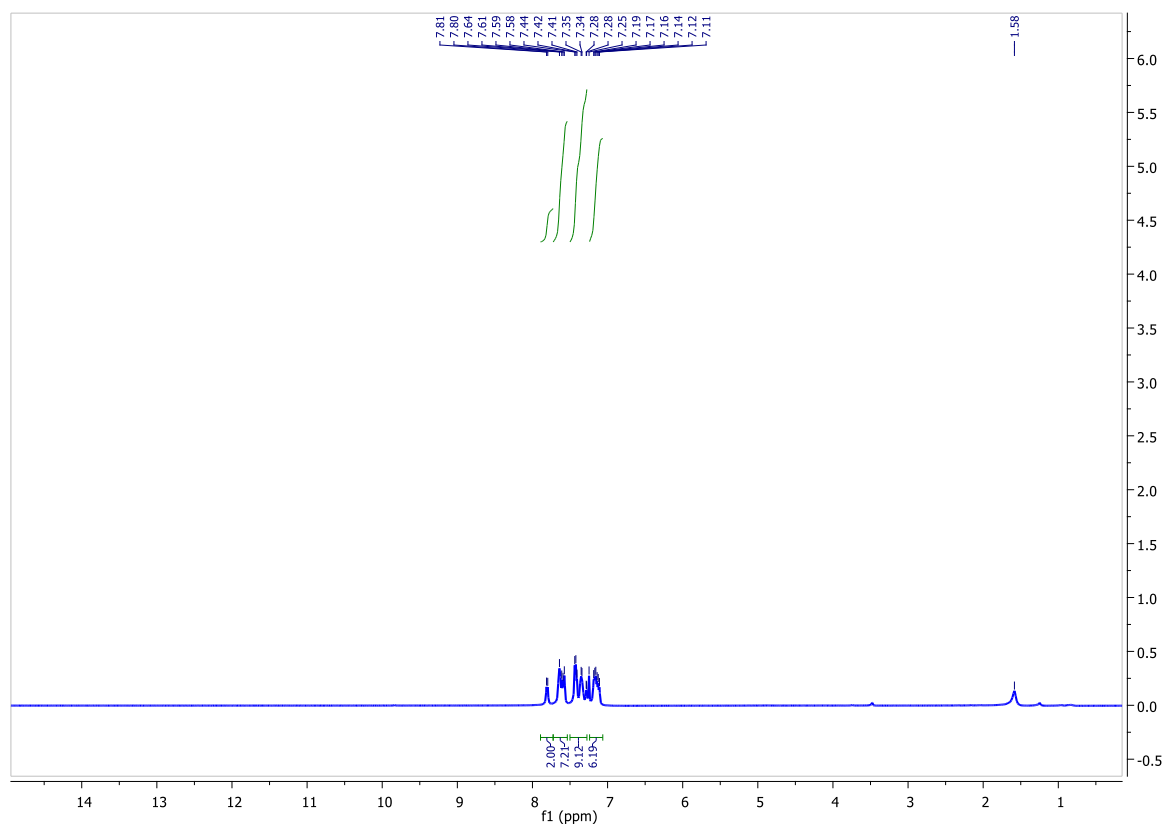


**Figure S8.**  $^1\text{H}$  NMR of TPA-Th-(CN) $_2$  ( $\text{CDCl}_3$ , 500 MHz, RT)

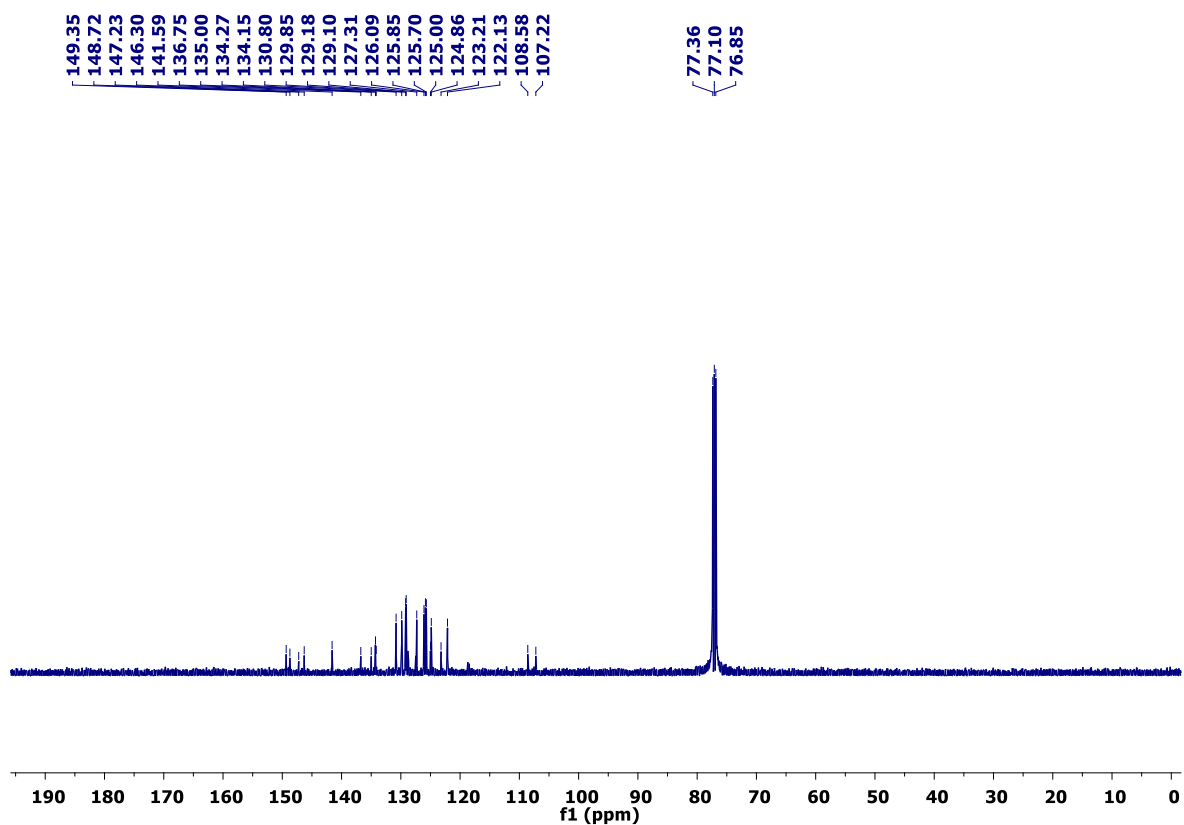


**Figure S9.**  $^{13}\text{C}$  NMR of **TPA-Th-(CN)<sub>2</sub>** ( $\text{CDCl}_3$ , 500 MHz, RT)



**Figure S10.** HRMS data of **1**

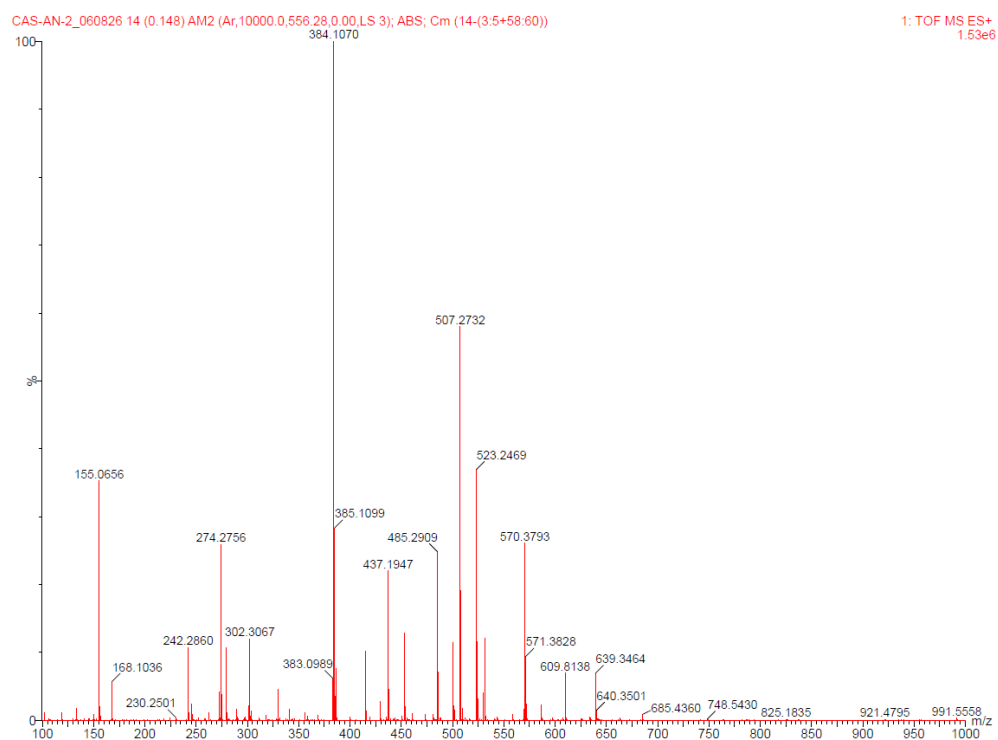


**Figure S11.** HRMS data of **2**

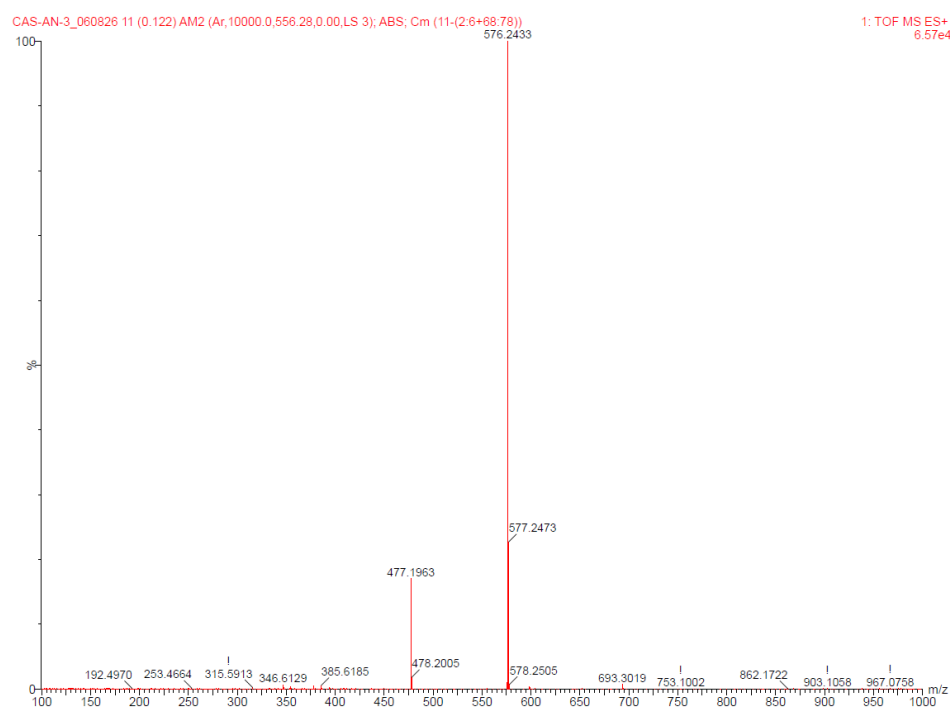


**Figure S12.** HRMS data of **TPA-Ph-(CN)<sub>2</sub>**

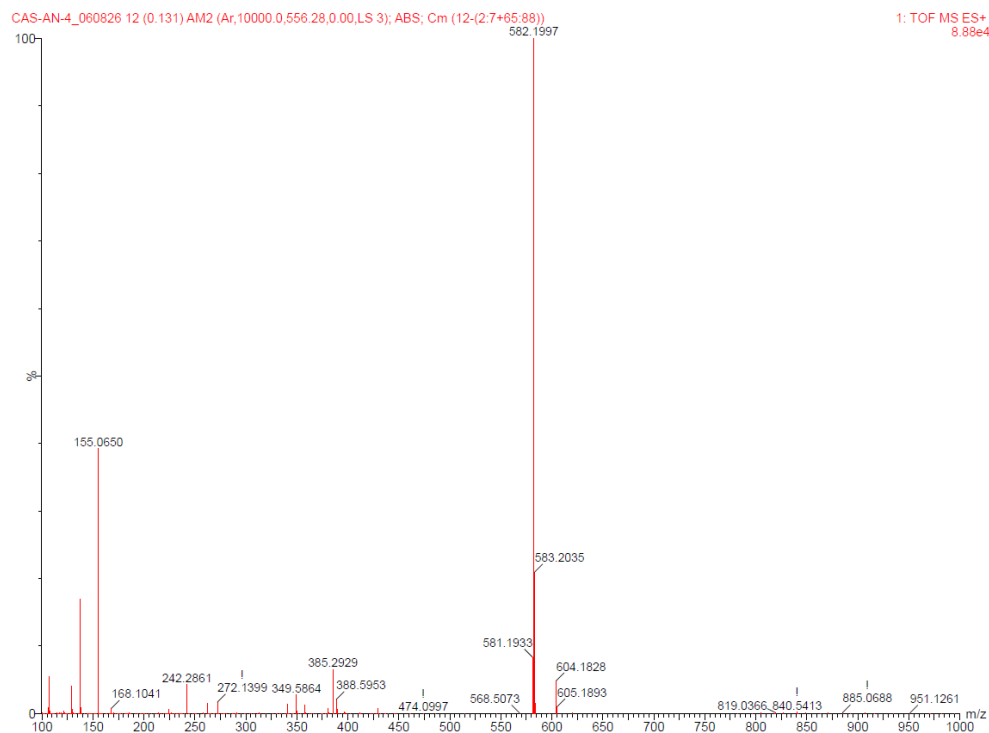


**Figure S13.** HRMS data of **TPA-Th-(CN)<sub>2</sub>**

### Photophysical properties

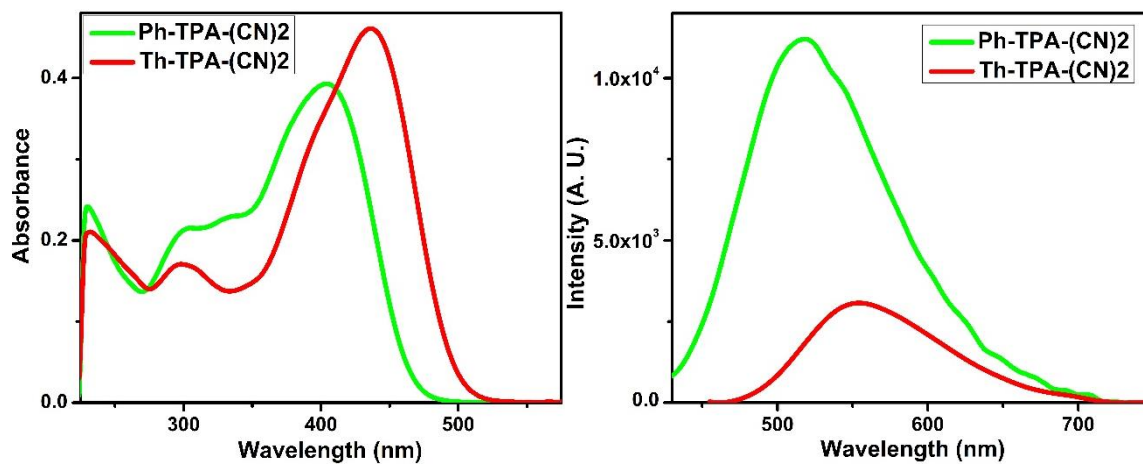


**Figure S14.** Absorption (left) and emission (right) spectra of **TPA-Ph-(CN)<sub>2</sub>** and **TPA-Th-(CN)<sub>2</sub>**

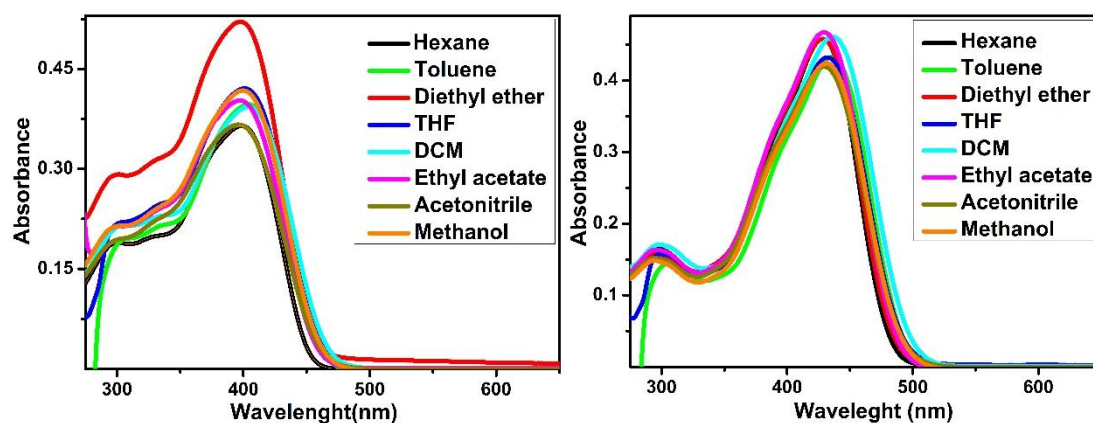


**Figure S15.** Absorption spectra of **TPA-Ph-(CN)2** (left) and **TPA-Th-(CN)2** (right) with different polarity of solvents

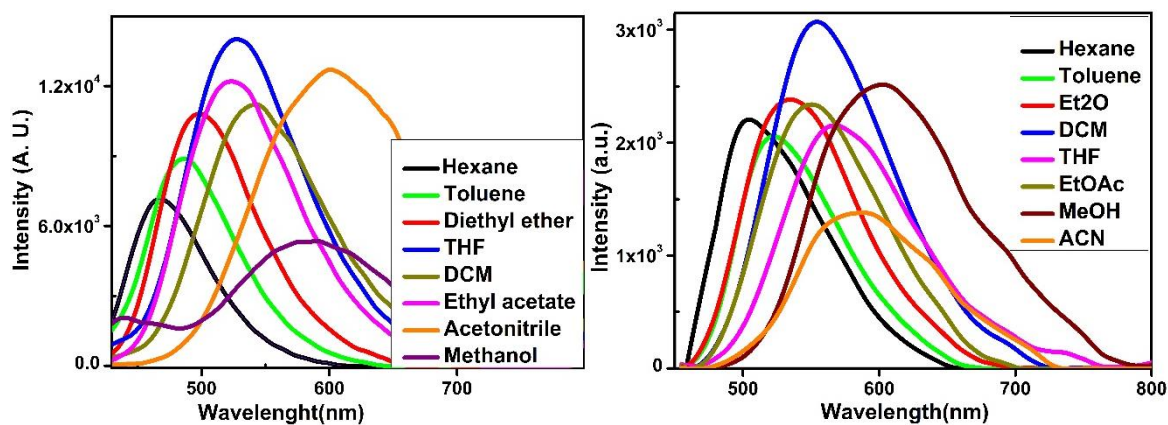


**Figure S16.** Emission spectra of **TPA-Ph-(CN)2** (left) and **TPA-Th-(CN)2** (right) with different polarity of solvents

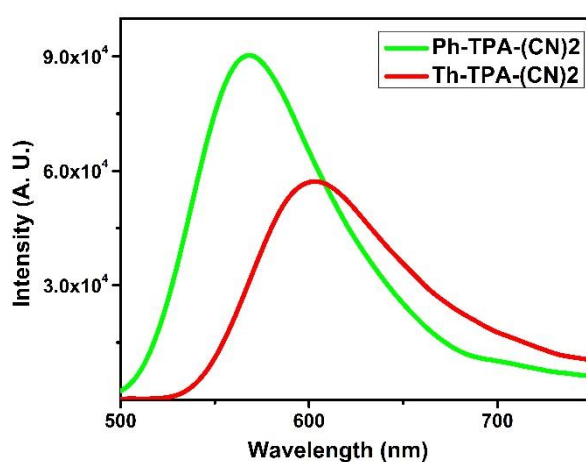


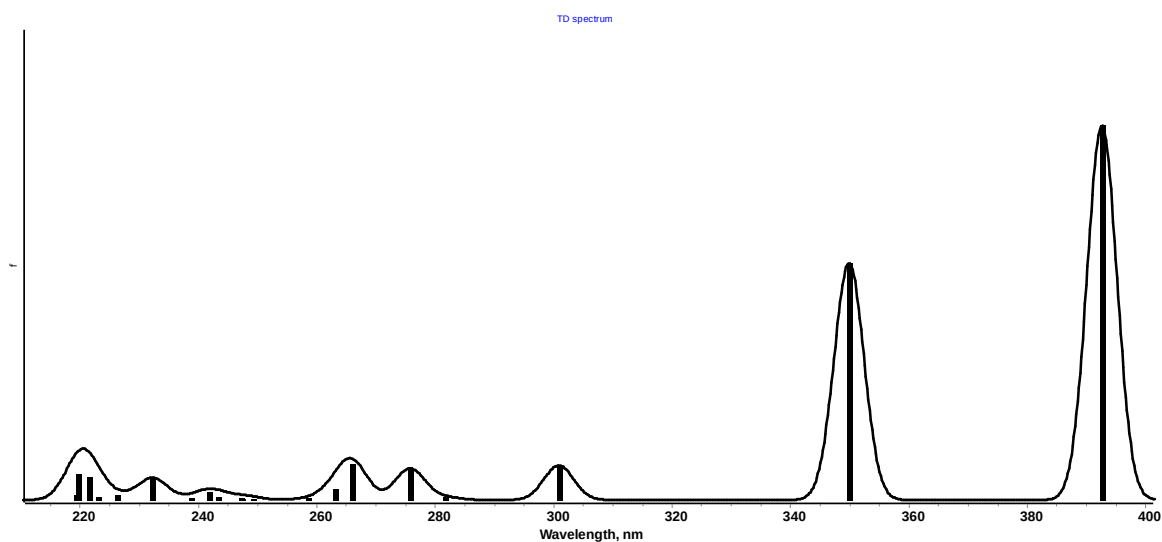
**Figure S17.** Solid state emission spectra of **TPA-Ph-(CN)2** and **TPA-Th-(CN)2**

**Table S1.** Optical properties of compounds **TPA-Ph-(CN)2** with different polarity solvents

| S. No | Solvents          | Absorption<br>( $\lambda$ , nm) | Emission<br>( $\lambda$ , nm) | Stoke shift<br>( $\Delta\nu$ , $\text{cm}^{-1}$ ) |
|-------|-------------------|---------------------------------|-------------------------------|---------------------------------------------------|
| 1     | Hexane            | 397                             | 467                           | 3775                                              |
| 2     | Toluene           | 404                             | 486                           | 4176                                              |
| 3     | Et <sub>2</sub> O | 398                             | 497                           | 5004                                              |
| 4     | THF               | 401                             | 526                           | 5926                                              |
| 5     | DCM               | 405                             | 540                           | 6172                                              |
| 6     | EtOAc             | 398                             | 523                           | 6005                                              |
| 7     | ACN               | 398                             | 600                           | 8458                                              |
| 8     | MeOH              | 400                             | 590                           | 8050                                              |

**Table S1.** Optical properties of compounds **TPA-Th-(CN)2** with different polarity solvents

| S. No | Solvents          | Absorption<br>( $\lambda$ , nm) | Emission<br>( $\lambda$ , nm) | Stoke shift<br>( $\Delta\nu$ , $\text{cm}^{-1}$ ) |
|-------|-------------------|---------------------------------|-------------------------------|---------------------------------------------------|
| 1     | Hexane            | 428                             | 504                           | 3523                                              |
| 2     | Toluene           | 436                             | 523                           | 3815                                              |
| 3     | Et <sub>2</sub> O | 428                             | 534                           | 4637                                              |
| 4     | THF               | 431                             | 566                           | 5534                                              |
| 5     | DCM               | 436                             | 554                           | 4885                                              |
| 6     | EtOAc             | 429                             | 550                           | 5128                                              |
| 7     | ACN               | 430                             | 586                           | 6190                                              |
| 8     | MeOH              | 431                             | 605                           | 6672                                              |

**Figure S18.** Simulated absorption spectra of compound **TPA-Ph-(CN)2** using M06-2X functional with 6-31G (d, p)/PCM (dichloromethane) model.

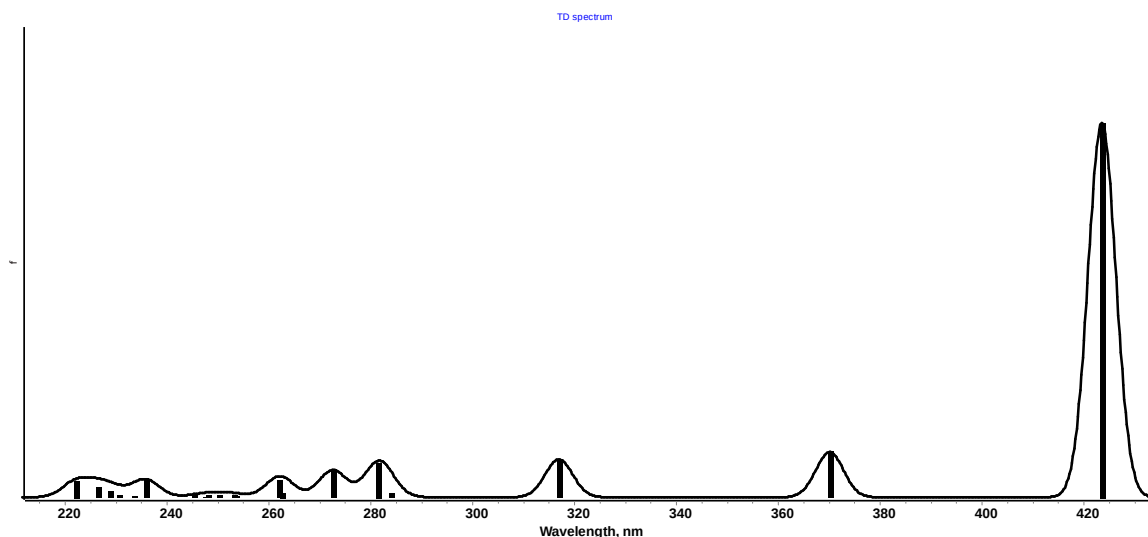


**Figure S19.** Simulated absorption spectra of compound **TPA-Th-(CN)<sub>2</sub>** using M06-2X functional with 6-31G (d, p)/PCM (dichloromethane) model.

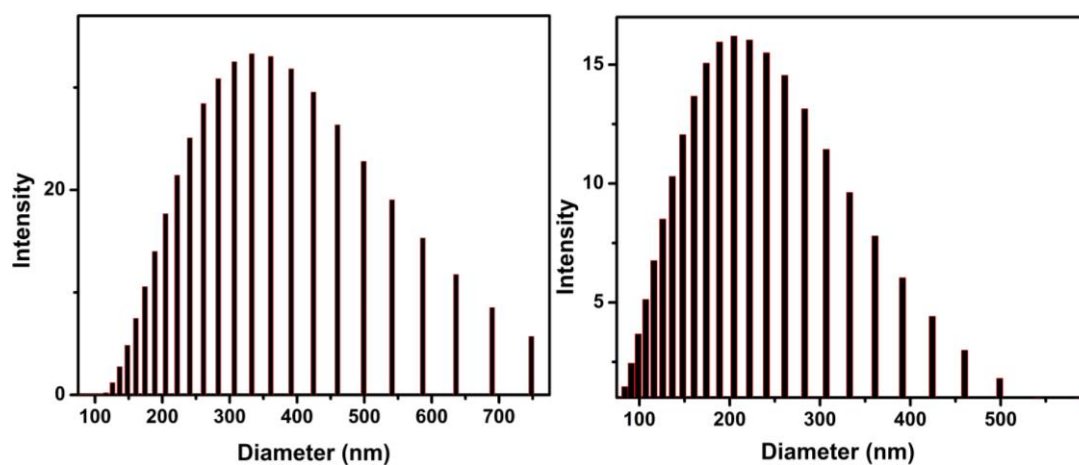


**Figure S20.** DLS data of **TPA-Ph-(CN)<sub>2</sub>** and **TPA-Th-(CN)<sub>2</sub>**

**Table S3.** DFT table of **TPA-Ph-(CN)<sub>2</sub>**

|   |              |             |              |
|---|--------------|-------------|--------------|
| 6 | -3.361329689 | 4.483946811 | 0.879968080  |
| 6 | -3.612435338 | 5.855422515 | 0.866132773  |
| 6 | -2.969201908 | 6.682347164 | -0.058076805 |
| 6 | -2.075879346 | 6.125862622 | -0.976650372 |
| 6 | -1.831011200 | 4.753056927 | -0.979665211 |
| 6 | -2.471683942 | 3.924550784 | -0.048115160 |
| 7 | -2.209025502 | 2.517627761 | -0.037271744 |
| 6 | -3.277524010 | 1.603873465 | -0.065661019 |
| 6 | -0.858656361 | 2.076362750 | -0.013829482 |

|   |               |              |              |
|---|---------------|--------------|--------------|
| 6 | -0.436463394  | 0.994577490  | -0.803924039 |
| 6 | 0.888543456   | 0.576307378  | -0.776182488 |
| 6 | 1.848800118   | 1.228510485  | 0.018996092  |
| 6 | 1.415376137   | 2.319210249  | 0.794775888  |
| 6 | 0.088701964   | 2.733309898  | 0.787705550  |
| 6 | -4.478566274  | 1.920088464  | -0.730379641 |
| 6 | -5.526995111  | 1.015333409  | -0.750000581 |
| 6 | -5.444611474  | -0.246083928 | -0.117718445 |
| 6 | -4.233664980  | -0.550231402 | 0.545568668  |
| 6 | -3.181632060  | 0.350192503  | 0.574672739  |
| 6 | -6.605406115  | -1.112200315 | -0.216954983 |
| 6 | -6.896958913  | -2.335362485 | 0.319278549  |
| 6 | -8.166747557  | -3.055162248 | 0.023492317  |
| 6 | -8.839954576  | -2.868843463 | -1.197483044 |
| 6 | -10.042509716 | -3.523958489 | -1.454663934 |
| 6 | -10.591521322 | -4.391619955 | -0.507423373 |
| 6 | -9.922246777  | -4.601137817 | 0.699711423  |
| 6 | -8.722081296  | -3.942630950 | 0.962292042  |
| 6 | 3.260464791   | 0.785797115  | 0.035556047  |
| 6 | 4.312622946   | 1.704393203  | 0.205728713  |
| 6 | 5.633970514   | 1.281117477  | 0.223167509  |
| 6 | 5.978654931   | -0.078397569 | 0.061158215  |
| 6 | 4.921625625   | -0.999572695 | -0.102221197 |
| 6 | 3.600896490   | -0.573315013 | -0.113314630 |
| 6 | 7.397426180   | -0.407633421 | 0.090578974  |
| 6 | 8.076804093   | -1.563829274 | -0.160624144 |
| 6 | 9.556021619   | -1.668685560 | -0.021351893 |
| 6 | 10.286858263  | -2.569969180 | -0.815088706 |
| 6 | 11.673846491  | -2.653589595 | -0.705606769 |
| 6 | 12.358742929  | -1.844217183 | 0.202568941  |
| 6 | 11.641866510  | -0.955981016 | 1.007940649  |
| 6 | 10.254912097  | -0.872892483 | 0.903938243  |

|   |               |              |              |
|---|---------------|--------------|--------------|
| 6 | -6.009640058  | -3.000821931 | 1.223303693  |
| 7 | -5.322526843  | -3.577725216 | 1.968294744  |
| 6 | 7.417170682   | -2.754913486 | -0.606550477 |
| 7 | 6.931032371   | -3.746234969 | -0.980063830 |
| 1 | -3.848743037  | 3.842795783  | 1.607115756  |
| 1 | -4.302488016  | 6.279307514  | 1.589482003  |
| 1 | -3.161627244  | 7.750669456  | -0.061639551 |
| 1 | -1.575127658  | 6.759342665  | -1.702613580 |
| 1 | -1.145998093  | 4.317620570  | -1.699724960 |
| 1 | -1.146849661  | 0.490416483  | -1.449918685 |
| 1 | 1.189443794   | -0.245385841 | -1.418323316 |
| 1 | 2.117850495   | 2.829057066  | 1.446521335  |
| 1 | -0.221568674  | 3.562620274  | 1.413861113  |
| 1 | -4.578049888  | 2.871913215  | -1.238920925 |
| 1 | -6.437063137  | 1.280180246  | -1.281356755 |
| 1 | -4.110468061  | -1.496648407 | 1.055837175  |
| 1 | -2.273293036  | 0.088729004  | 1.105016993  |
| 1 | -7.399249301  | -0.692220575 | -0.829740967 |
| 1 | -8.409534925  | -2.229854913 | -1.961731797 |
| 1 | -10.542904485 | -3.368232351 | -2.405786086 |
| 1 | -11.524865632 | -4.906606416 | -0.713143481 |
| 1 | -10.335234112 | -5.276861508 | 1.442639846  |
| 1 | -8.215293907  | -4.110627560 | 1.907567807  |
| 1 | 4.094116288   | 2.762948873  | 0.301709450  |
| 1 | 6.425229040   | 2.014610469  | 0.350979691  |
| 1 | 5.125467189   | -2.057549192 | -0.202905131 |
| 1 | 2.813607651   | -1.313938949 | -0.209879918 |
| 1 | 8.029166287   | 0.440314754  | 0.342546103  |
| 1 | 9.767279284   | -3.202151998 | -1.528446493 |
| 1 | 12.218862491  | -3.351797477 | -1.333608272 |
| 1 | 13.438691669  | -1.912056019 | 0.290229721  |
| 1 | 12.161401197  | -0.336045856 | 1.732380467  |

|   |             |              |             |
|---|-------------|--------------|-------------|
| 1 | 9.711377105 | -0.205490041 | 1.564846014 |
|---|-------------|--------------|-------------|

**Table S4.** DFT table of **TPA-Th-(CN)2**

|   |              |              |              |
|---|--------------|--------------|--------------|
| 6 | 1.091881872  | 3.954086156  | 0.947030491  |
| 6 | 1.110843023  | 5.346958110  | 0.886225067  |
| 6 | 1.840659429  | 6.001098238  | -0.109271389 |
| 6 | 2.546737405  | 5.250716384  | -1.052532945 |
| 6 | 2.519593649  | 3.857347020  | -1.009058542 |
| 6 | 1.795315527  | 3.201623562  | -0.003671409 |
| 7 | 1.765094765  | 1.771303401  | 0.048234947  |
| 6 | 2.967826877  | 1.041719435  | -0.005224542 |
| 6 | 0.510258448  | 1.117594716  | 0.139939848  |
| 6 | -0.593699535 | 1.589049332  | -0.589683730 |
| 6 | -1.827884085 | 0.961669629  | -0.486996290 |
| 6 | -2.013989770 | -0.161700005 | 0.341858750  |
| 6 | -0.900146757 | -0.622452873 | 1.073358800  |
| 6 | 0.334663483  | 0.002782998  | 0.978846479  |
| 6 | 3.027829063  | -0.222620456 | -0.622687478 |
| 6 | 4.222268047  | -0.922865659 | -0.668067777 |
| 6 | 5.418798366  | -0.404416135 | -0.123110681 |
| 6 | 5.343068498  | 0.864107220  | 0.495705049  |
| 6 | 4.150506972  | 1.566220096  | 0.556151419  |
| 6 | 6.611560181  | -1.224550895 | -0.239710411 |
| 6 | 7.926328309  | -0.984936468 | 0.046331209  |
| 6 | 8.982522970  | -2.021001628 | -0.123761568 |
| 6 | 8.686156352  | -3.388837942 | 0.015637073  |
| 6 | 9.673188235  | -4.353909784 | -0.174340979 |
| 6 | 10.979825607 | -3.975242938 | -0.491625358 |
| 6 | 11.291151378 | -2.619586929 | -0.612293019 |
| 6 | 10.304905747 | -1.652117317 | -0.427796304 |
| 6 | -3.305389748 | -0.836863519 | 0.453746377  |
| 6 | -3.566271777 | -2.116809280 | 0.913346935  |
| 6 | -4.933066427 | -2.453533263 | 0.893339908  |

|    |               |              |              |
|----|---------------|--------------|--------------|
| 6  | -5.760983532  | -1.445003903 | 0.416203834  |
| 16 | -4.795088470  | -0.034680006 | -0.005058882 |
| 6  | -7.182303086  | -1.575829648 | 0.301831142  |
| 6  | -8.145955706  | -0.709924152 | -0.140158106 |
| 6  | -9.587275568  | -1.065299261 | -0.202941226 |
| 6  | -10.005598544 | -2.404279513 | -0.314539286 |
| 6  | -11.360395279 | -2.726525449 | -0.342183841 |
| 6  | -12.328503625 | -1.721332230 | -0.274852443 |
| 6  | -11.926384585 | -0.387671596 | -0.184565201 |
| 6  | -10.571650928 | -0.061956719 | -0.151005132 |
| 6  | 8.385931397   | 0.291772611  | 0.501454392  |
| 7  | 8.811041231   | 1.314915154  | 0.865106804  |
| 6  | -7.801213556  | 0.613283940  | -0.557733416 |
| 7  | -7.554661356  | 1.699447973  | -0.903626261 |
| 1  | 0.536096411   | 3.445130685  | 1.727666508  |
| 1  | 0.563260439   | 5.921249201  | 1.627380048  |
| 1  | 1.858346126   | 7.085672622  | -0.150019695 |
| 1  | 3.110807019   | 5.749473186  | -1.834862335 |
| 1  | 3.055413322   | 3.273807223  | -1.750419034 |
| 1  | -0.476554593  | 2.442936261  | -1.247510964 |
| 1  | -2.652562096  | 1.335483740  | -1.086406475 |
| 1  | -1.010610401  | -1.459880076 | 1.754117914  |
| 1  | 1.167436371   | -0.360914182 | 1.570560403  |
| 1  | 2.137793915   | -0.646871434 | -1.072596621 |
| 1  | 4.242153851   | -1.893149738 | -1.156678335 |
| 1  | 6.218721376   | 1.302741786  | 0.956286526  |
| 1  | 4.123510174   | 2.529367992  | 1.052599045  |
| 1  | 6.414912571   | -2.210396335 | -0.653849657 |
| 1  | 7.686044320   | -3.699811852 | 0.299804862  |
| 1  | 9.423204056   | -5.404202917 | -0.057640049 |
| 1  | 11.748860012  | -4.728510289 | -0.632449766 |
| 1  | 12.304155492  | -2.311664176 | -0.853353375 |

|   |               |              |              |
|---|---------------|--------------|--------------|
| 1 | 10.559713906  | -0.601692312 | -0.529135572 |
| 1 | -2.789402576  | -2.801406739 | 1.230886088  |
| 1 | -5.321517914  | -3.416439499 | 1.206480825  |
| 1 | -7.538125361  | -2.543593658 | 0.645591084  |
| 1 | -9.271913180  | -3.198502718 | -0.406552064 |
| 1 | -11.660020941 | -3.766345763 | -0.432294386 |
| 1 | -13.383661416 | -1.975070049 | -0.302945293 |
| 1 | -12.667832397 | 0.404143985  | -0.136961972 |
| 1 | -10.273785362 | 0.979088186  | -0.073938251 |

**Table S5.** Computed singlet vertical transitions involved in Compound **Ph-TPA-(CN)2** from TD-DFT calculation using M06-2X functional with 6-31G (d, p)/PCM (dichloromethane) model in Gaussian09

| Excited States | E (eV)    | $\lambda_{\text{max}}$ (nm) | $f^a$  | Major transitions (%)                                                      |
|----------------|-----------|-----------------------------|--------|----------------------------------------------------------------------------|
| S <sub>1</sub> | 3.1581 eV | 392.58 nm                   | 1.7028 | HOMO→LUMO (26.68 %)<br>HOMO→LUMO+1 (16.49 %)                               |
| S <sub>2</sub> | 3.5436 eV | 349.88 nm                   | 1.0775 | HOMO-1→LUMO+1 (12.85 %)<br>HOMO→LUMO+1 (9.09 %)<br>HOMO→LUMO+2 (24.36 %)   |
| S <sub>3</sub> | 4.1208 eV | 300.87 nm                   | 0.1569 | HOMO-1→LUMO (24.18 %)<br>HOMO→LUMO (6.80 %)                                |
| S <sub>4</sub> | 4.4009 eV | 281.73 nm                   | 0.0124 | HOMO→LUMO+2 (7.16 %)<br>HOMO→LUMO+3 (30.13 %)                              |
| S <sub>5</sub> | 4.4968 eV | 275.72 nm                   | 0.1431 | HOMO-2→LUMO (7.77 %)<br>HOMO-2→LUMO+1 (19.01 %)<br>HOMO-1→LUMO+1 (14.29 %) |

**Table S6.** Computed singlet vertical transitions involved in Compound **Th-TPA-(CN)2** from TD-DFT calculation using M06-2X functional with 6-31G (d, p)/PCM (dichloromethane) model in Gaussian09

| Excited States | E (eV)    | $\lambda_{\text{max}}$ (nm) | $f^a$  | Major transitions (%)                              |
|----------------|-----------|-----------------------------|--------|----------------------------------------------------|
| S <sub>1</sub> | 2.9278 eV | 423.48 nm                   | 2.1942 | HOMO→LUMO (38.49 %)                                |
| S <sub>2</sub> | 3.3506 eV | 370.04 nm                   | 0.2642 | HOMO-1→LUMO (9.08 %)<br>HOMO→LUMO+1 (35.44 %)      |
| S <sub>3</sub> | 3.9124 eV | 316.90 nm                   | 0.2226 | HOMO-1→LUMO (29.48 %)<br>HOMO→LUMO (5.43 %)        |
| S <sub>4</sub> | 4.3648 eV | 284.06 nm                   | 0.0218 | HOMO→LUMO+3 (37.75 %)                              |
| S <sub>5</sub> | 4.3188 eV | 287.08 nm                   | 0.0006 | HOMO-2→LUMO+1 (14.13 %)<br>HOMO-1→LUMO+1 (16.65 %) |