

# **Synthesis and photophysical properties of a new tetraphenylethylene-*o*-carborane-based star-shaped molecule**

Xiang Li<sup>\*a</sup>, Qin Zhou<sup>a</sup>, Miao Zhu<sup>a</sup>, Wei Chen<sup>a</sup>, Beibei Wang<sup>a</sup>, Ye Sha<sup>\*b</sup>, and Hong Yan<sup>\*c</sup>

[a] Jiangsu Key Laboratory of Pesticide Science and Department of Chemistry, College of Sciences, Nanjing Agricultural University, Nanjing 210095, China

[b] Department of Chemistry and Material Science, College of Science, Nanjing Forestry University, Nanjing 210037, China

[c] State Key Laboratory of Coordination Chemistry, School of Chemistry and Chemical Engineering, Nanjing University, Nanjing, Jiangsu 210023, China

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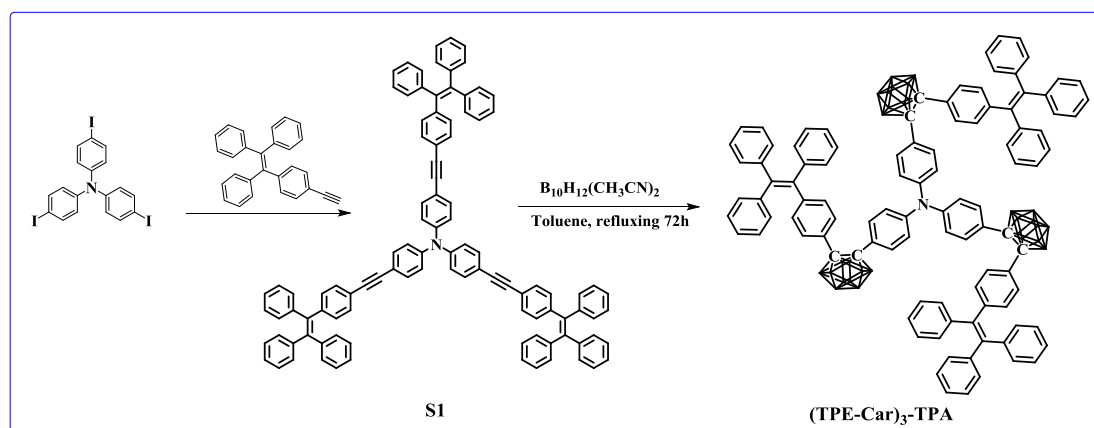
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## I. General method

In this work, all the synthetic steps were carried out under an inert argon atmosphere using standard Schlenk and glovebox techniques. Commercial reagents were used without any further purification after purchasing. THF and toluene were distilled on sodium / benzophenone. tris(4-iodophenyl)amine <sup>[S1]</sup> (2-(4-ethynylphenyl)ethene-1,1,2-triyl)tribenzene, <sup>[S2]</sup> and **S1** were synthesized according to literature procedures. <sup>[S3]</sup> B<sub>10</sub>H<sub>12</sub>(CH<sub>3</sub>CN)<sub>2</sub> was synthesized by a modified method according to literature reports. <sup>[S4]</sup> NMR spectra (<sup>1</sup>H-, <sup>13</sup>C-, and <sup>11</sup>B-) were recorded on DRX-400 at ambient temperature. CDCl<sub>3</sub> was used as deuterated reagent unless specified. Mass spectra were measured with ESI-MS (LCQ Fleet, Thermo Fisher Scientific) and MALDI-TOF MS. Infrared spectra were performed on a Nicolet NEXUS870 FT-IR. UV-VIS absorption spectra were recorded with Shimadzu UV-3600 spectrophotometers. FL and PL spectra were recorded on a Hitachi F-7000 fluorescence spectrophotometer.

## II. Synthesis



**Scheme S1.** Synthetic routes towards  $(TPE-Car)_3-TPA$ .

### Synthesis of tris(4-((4-(1,2,2-triphenylvinyl)phenyl)ethynyl)phenyl)amine (**S1**):

To a mixture of *tris*(4-iodophenyl)amine (250 mg, 0.40 mmol),  $Pd(PPh_3)_2Cl_2$  (30 mg, 0.04 mmol), and copper iodide (8 mg, 0.04 mmol) was added THF (20 mL) under nitrogen and the suspension was stirred at room temperature for 15 min. Triethylamine (4 mL) was added to the reaction mixture and stirred for 0.5 h at room temperature. To the reaction mixture was added dropwise a solution of 1-(4-ethynylphenyl)-1,2,2-triphenylethylene (400 mg, 1.12 mmol) in THF (8 mL). The reaction mixture was stirred under nitrogen at room temperature for 24 h, solvent was removed in a rotary evaporator and the crude product was purified using column chromatography (silica gel/DCM: hexane 1:3) to yield the star-shaped molecule **1** (392 mg, 75%) as yellow solids.  $^1H$  NMR (500 MHz,  $CDCl_3$ ): 7.45 – 7.33 (m, 7H), 7.12 (m, 28H), 7.04 (m, 34H).  $^{13}C$  NMR (125 MHz,  $CDCl_3$ ): 146.56, 143.80, 143.50, 143.43, 143.34, 141.60, 140.27, 132.70, 131.36, 131.30, 131.28, 130.83, 127.80, 127.72, 127.64, 126.64, 126.57, 123.96, 121.14, 117.97, 89.48 (yne-C). MALDI-TOF MS: calcd for  $C_{102}H_{69}N$ , 1308.68; found 1308.4.

### Synthesis of $(TPE-Car)_3-TPA$ .

To a toluene solution (50 mL) of tris(4-((4-(1,2,2-triphenylvinyl)phenyl)ethynyl)phenyl)amine (**1**) (200 mg, 0.15 mmol),  $B_{10}H_{12}(CH_3CN)_2$  (0.28 g, 1.35 mmol, 9 equiv) was added at room temperature.

The resulting reaction mixture was refluxed for 24h. MeOH (30 mL) was then added to quench the reaction. Excessive solvent was removed under vacuum, and the resulting red solid was filtered and dissolved in toluene. Then the toluene solution was passed through an alumina column. After removal of solvent, a yellow-white solid was afforded. The crude product was purified by column chromatography (silica gel) using hexane / CH<sub>2</sub>Cl<sub>2</sub> (V / V = 3:1) as eluent to afford **(TPE-Car)<sub>3</sub>-TPA** as a yellow solid (74 mg, 30%). <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm): 7.23 (d, J = 8.5 Hz, 6H), 7.07 (d, J = 19.2 Hz, 24H), 6.98 – 6.87 (m, 27H), 6.82 (d, J = 8.0 Hz, 6H), 6.71 (d, J = 8.2 Hz, 6H), 3.25–1.70 (br, 30H, B-H). <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>) δ (ppm): 13C NMR (101 MHz, CDCl<sub>3</sub>) δ 147.30, 145.96, 143.04, 142.92, 142.51, 139.04, 132.00, 131.19, 131.14, 129.94, 128.51, 127.89, 127.79, 127.73, 126.92, 126.90, 126.81, 126.30, 122.99, 85.10 (Cb-C), and 84.39 (Cb-C). <sup>11</sup>B-NMR (160 MHz, CDCl<sub>3</sub>) δ (ppm): -2.0 (12B), -9.9 (18B). MALDI-TOF MS: calcd for C<sub>102</sub>H<sub>99</sub>NB<sub>30</sub>, 1663.2; found 1663.8.

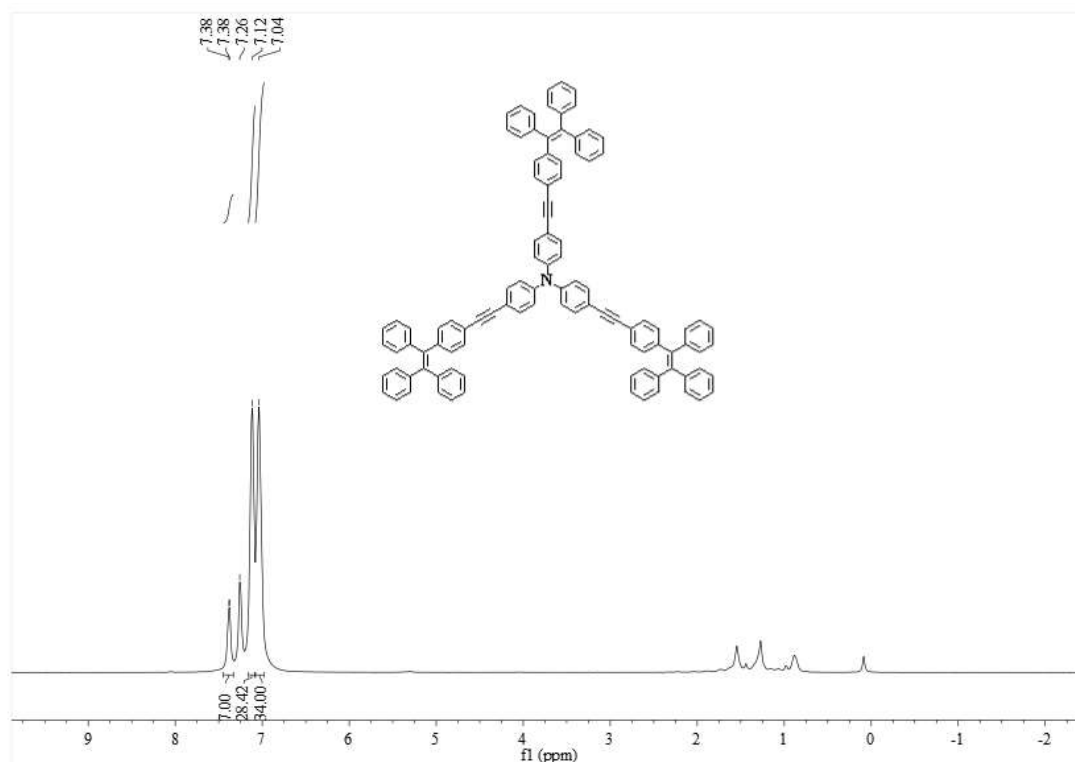


Figure.S1. The <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>) spectrum of compound S1.

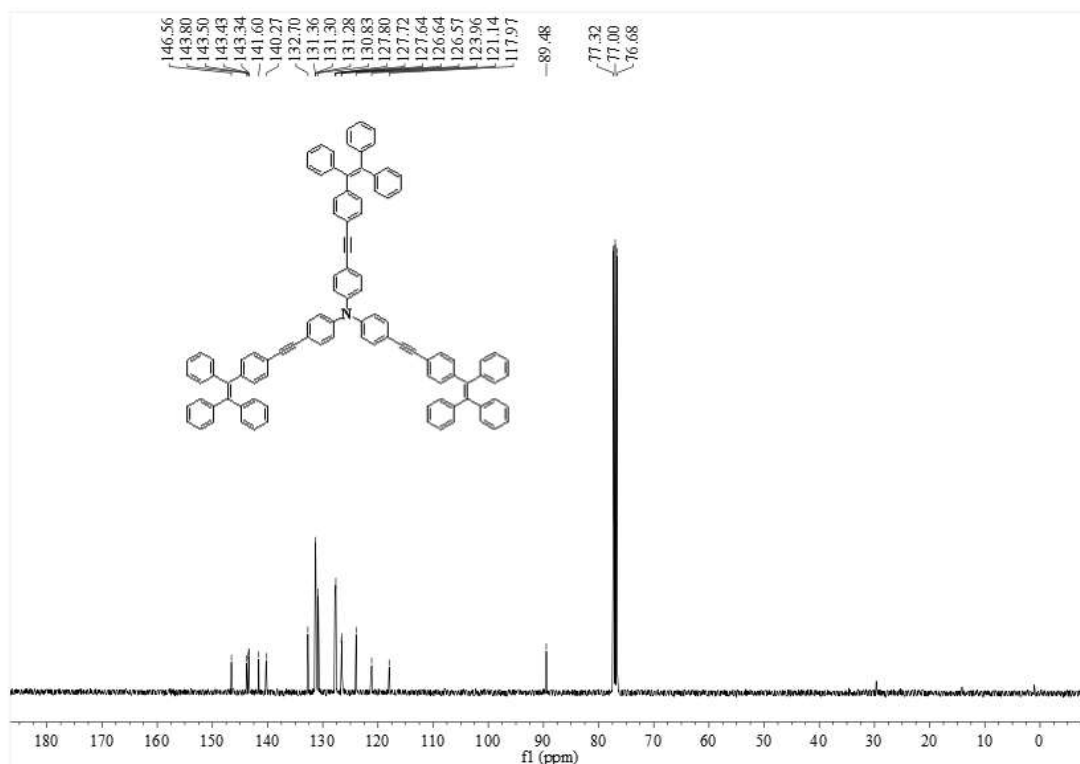


Figure.S2. The  $^{13}\text{C}$ -NMR (100 MHz,  $\text{CDCl}_3$ ) spectrum of compound S1.

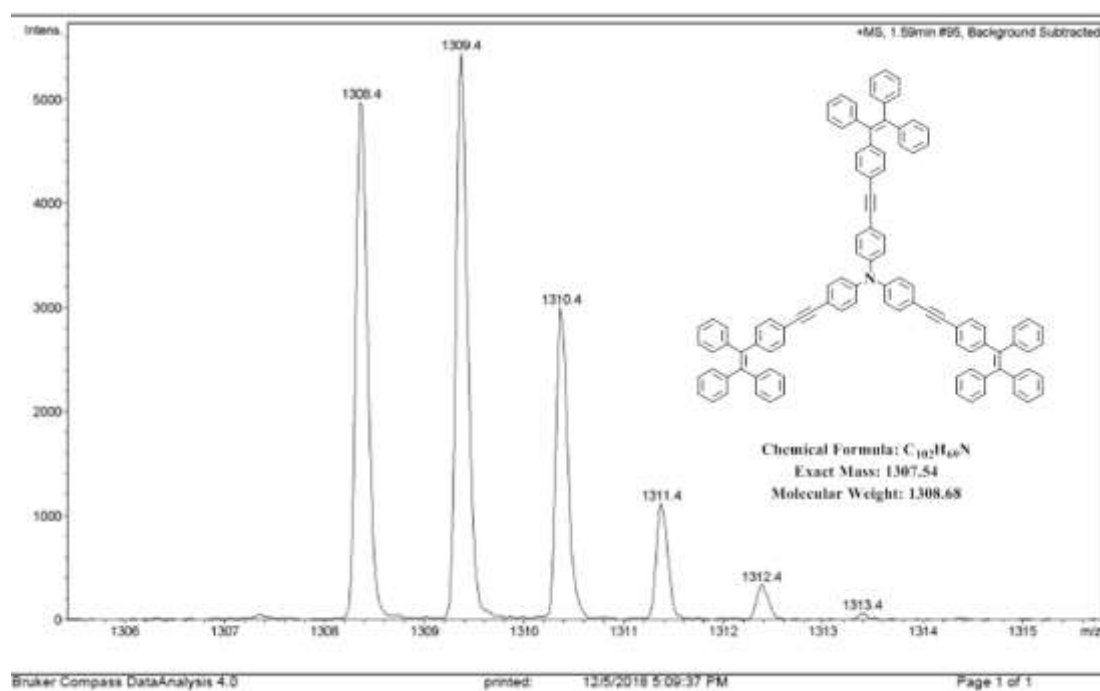


Figure.S3. The MALDI-TOF MS spectrum of compound S1.

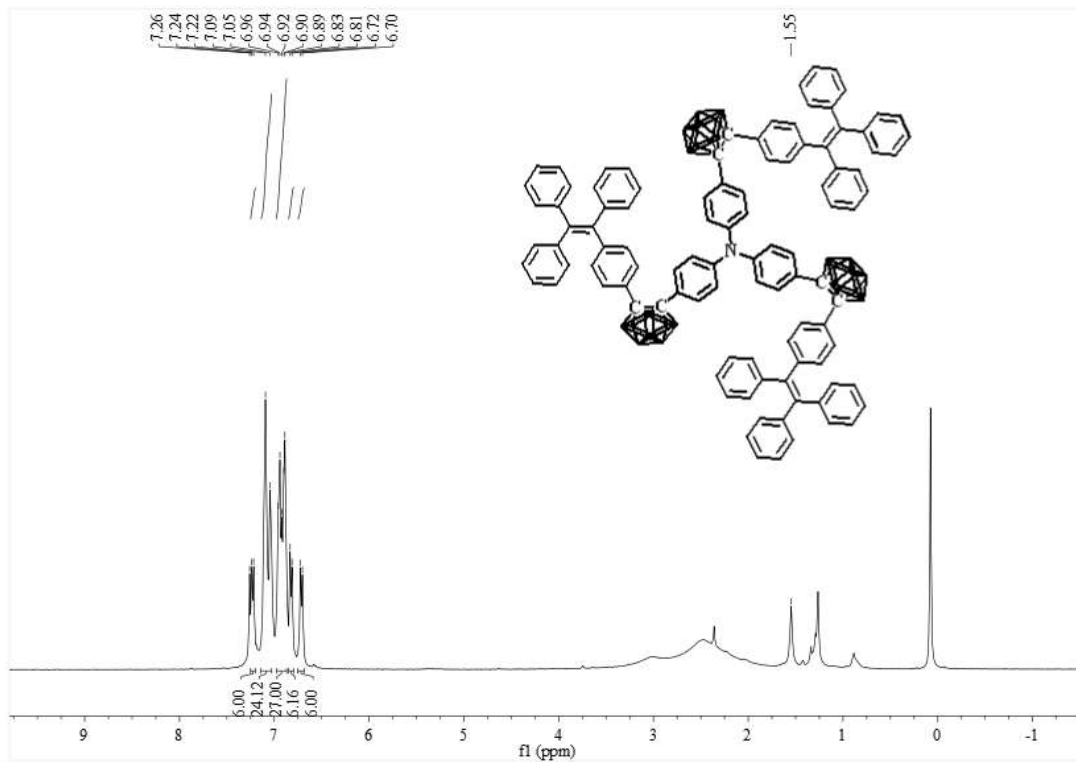


Figure.S4. The <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>) spectrum of compound (TPE-Car)<sub>3</sub>-TPA.

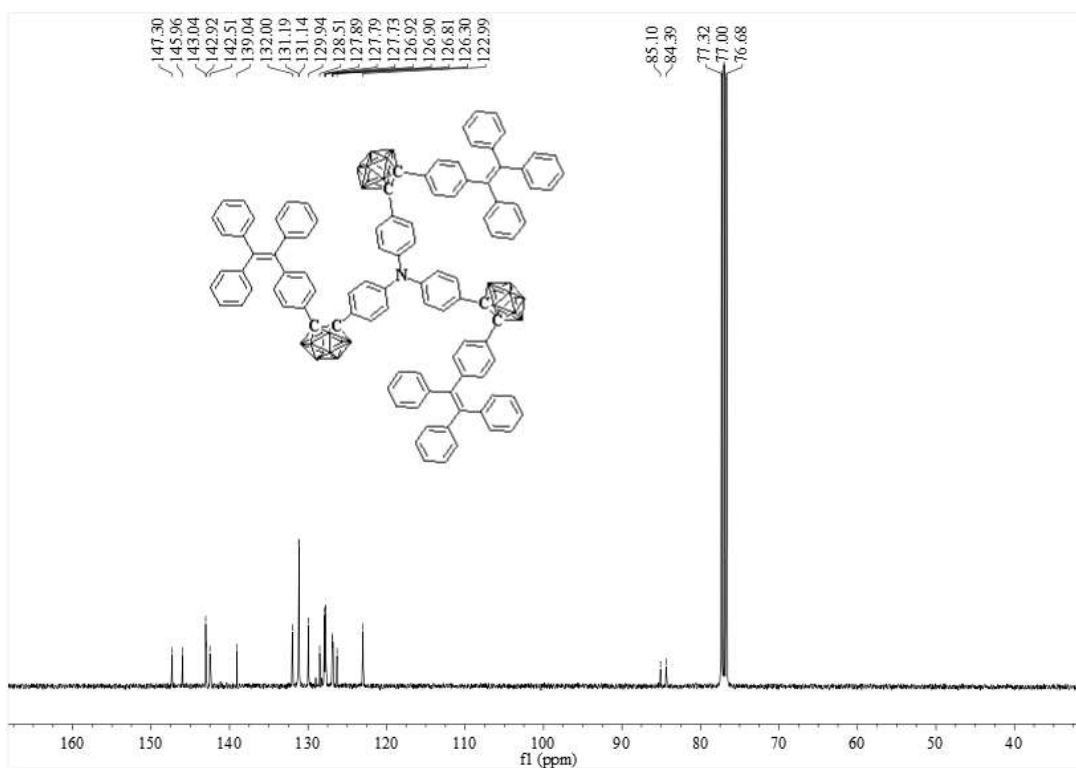


Figure.S5. The <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>) spectrum of compound (TPE-Car)<sub>3</sub>-TPA.

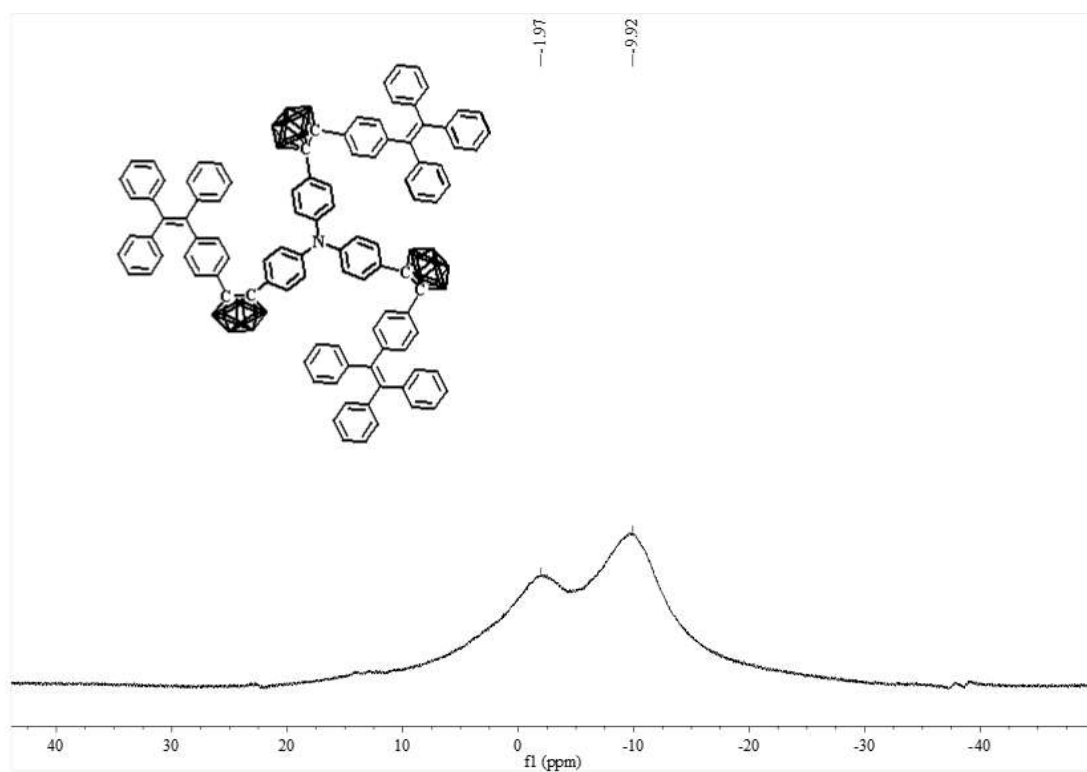


Figure.S6. The  $^{11}\text{B}$ -NMR (160 MHz,  $\text{CDCl}_3$ ) spectrum of compound **(TPE-Car)<sub>3</sub>-TPA**.

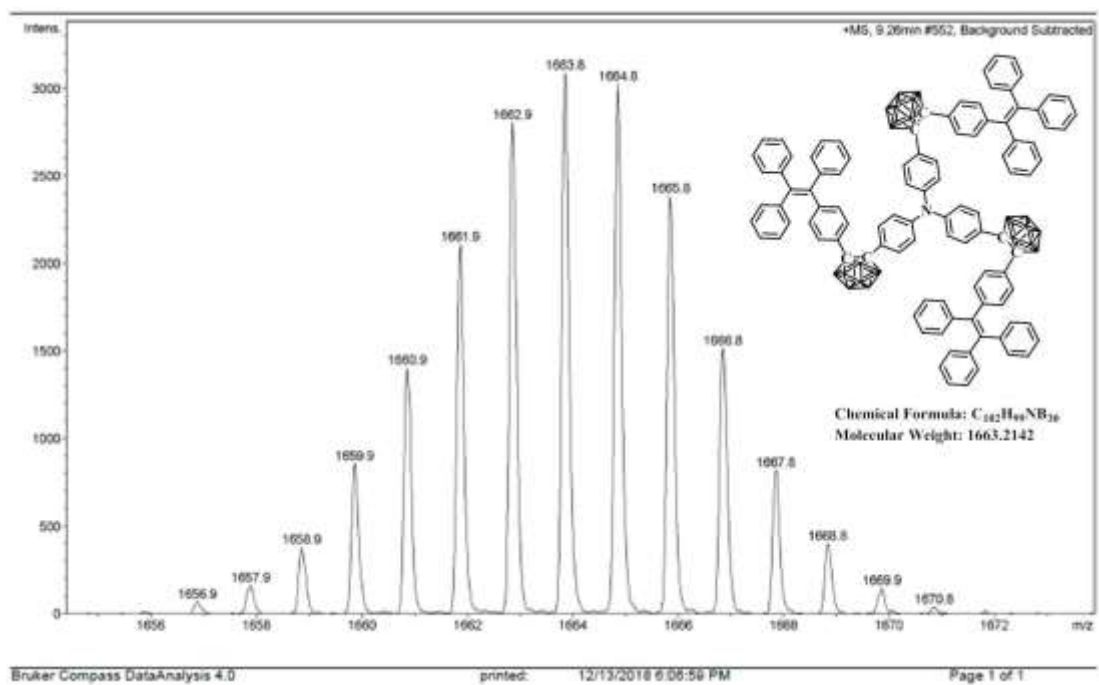


Figure.S7. The MALDI-TOF MS spectrum of compound **(TPE-Car)<sub>3</sub>-TPA**.

**III. Quantum yields determination:** Absolute quantum yields of all compounds in THF/water or in solid state were measured by employing an integrating sphere.

#### The Principle of Absolute Quantum Yield Measurements

The absolute fluorescence quantum yield,  $\eta$ , is, by definition, the ratio of the number of photons emitted to the number of photons absorbed:

$$\eta = \frac{N^{em}}{N^{abs}} \quad (1)$$

There are two different methods for the measurement of the absolute fluorescence quantum yield: “Direct Excitation” measurements and “Direct & Indirect Excitation” measurements.

With “Direct Excitation” measurements one records the scatter and the emission of the sample being directly excited by the radiation from the excitation monochromator only, whereas with “Direct and Indirect Excitation” one also records the emission of the sample while it is in a position where it is only indirectly excited by excitation radiation bouncing within the sphere.

#### “Direct Excitation” Method

This method only requires two experimental setups, see figure 1.

Note that with the “Direct Excitation” method the emission measurement actually contains the information of both direct and indirect excitation, as photons that pass the sample in the direct excitation beam may still be absorbed after scattering in the sphere.

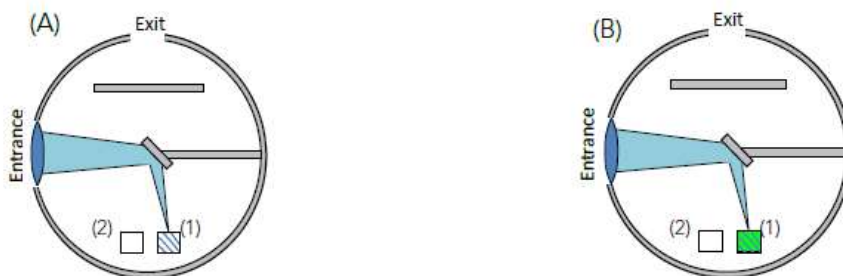


Figure 1. Two different measurement configurations required for Direct Excitation measurements: (A) reference sample (solvent only) in sample position (1); (B) test sample in position 1 (position 2 remains empty for both measurements.)



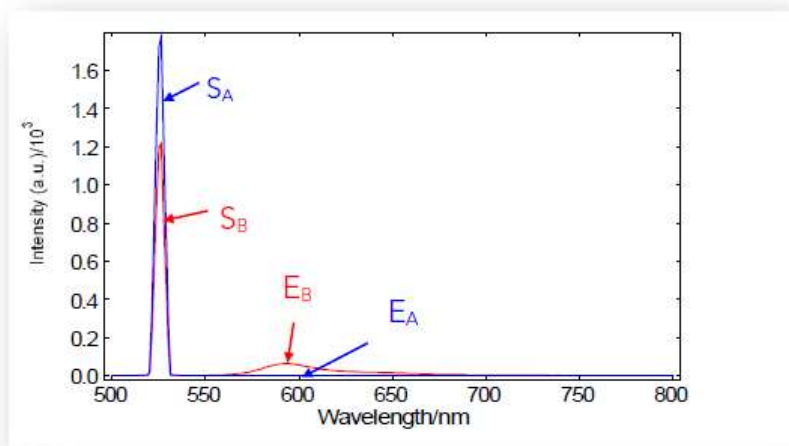


Figure 2. Spectral scans of the excitation scatter region or S-region (peaks on the left) and the emission region (E-region) of the sample and the solvent. The indices “A” and “B” refer to the experimental setup illustrated in Figure 1. Note that the quantities  $S_A$ ,  $S_B$ ,  $E_A$ , and  $E_B$  refer to the integral of the scans.

The absolute fluorescence quantum yield, calculated with the “Direct Excitation” method is calculated as follows:

$$\eta_{DExc} = \frac{E_B - E_A}{S_A - S_B} \quad (2)$$

$E_A(\lambda)$  and  $S_A(\lambda)$ , as well as  $E_B(\lambda)$  and  $S_B(\lambda)$  may be measured in four individual scans. However, it is often convenient to measure these spectra in two scans only. For the calculation of the integrals, the selection of the integral regions, and the final calculation of  $\eta_{DExc}$  use the quantum yield wizard that is supplied with the F980 software.

If the sphere background,  $E_A(\lambda)$ , is sufficiently low the measurement of this region may be omitted to save measurement time. In this case the equation degrades to:

$$\eta_{DExc} = \frac{E_B}{S_A - S_B} \quad (3)$$

**IV. Spectra data:** UV–VIS absorption spectra were recorded with Shimadzu UV–3600 spectrophotometers. FL and PL spectra were recorded on a Hitachi F–7000 fluorescence spectrophotometer.

## V. Quantum chemical calculations

Geometries of all complexes were optimized using density functional theory (DFT) method. The electronic transition energies including electron correlation effects were computed by TD–DFT method using B3LYP functional (TD–B3LYP). The 6–31G(d, p) basis set was used to treat all

atoms. All calculations described here were performed by using Gaussian 09 program.<sup>[S5]</sup>

## VI. Cyclic voltammetry (CV)

Electrochemical determination: Cyclic Volta metric experiments were carried out with an IM6ex (Zahner) using three electrode cell assemblies. All measurements were carried out in a one-compartment cell under Argon, equipped with a glassy-carbon working electrode, a platinum wire counter electrode, and a Ag / Ag<sup>+</sup> reference electrode under a scan rate of 100 mV s<sup>-1</sup>. The supporting electrolyte was a 0.10 mol L<sup>-1</sup> acetonitrile solution of tetrabutyl-ammonium hexafluorophosphate (Bu<sub>4</sub>NPF<sub>6</sub>). Each oxidation potential was calibrated with ferrocene as a reference.

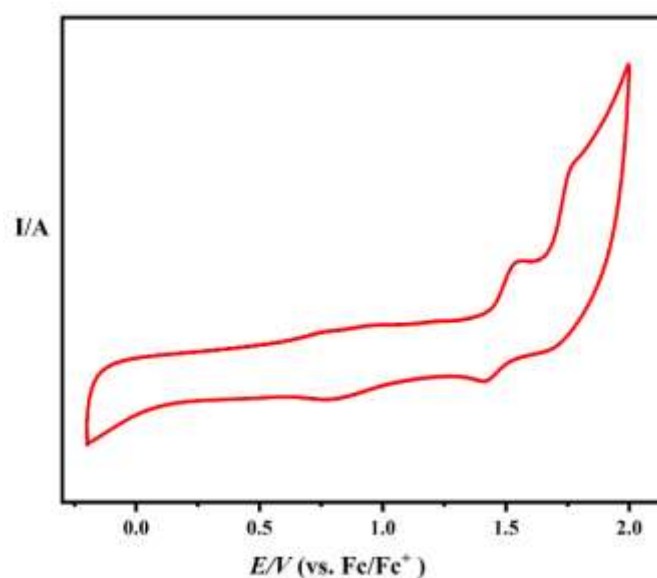


Figure.S8. Cyclic voltammograms of **(TPE-Car)<sub>3</sub>-TPA** at a scan rate of 100 mV s<sup>-1</sup> (in degassed CH<sub>2</sub>Cl<sub>2</sub> at 298 K).

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