

Supporting information for
Synthesis and characterization of novel 1, 4-bis (carbazolyl) benzene
derivatives with blue-violet two-photon-excited fluorescence

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Experimental Section

Synthetic Procedures. All chemicals used were of analytical reagent grade, which were obtained from commercial sources and used without further purification. (η^6 -1, 4-Dichlorobenzene) (η^5 -cyclopentadienyl) iron hexafluorophosphate (Fc-2Cl) were prepared through the ligand exchange reaction of ferrocene and dichlorobenzene according to the reference procedure.¹ 3,6-Dibromocarbazole and 3-bromocarbazole were prepared using a modified version of a previously reported method.^{2,3} Chromatographic purification of products was accomplished using 200-400 mesh chromatography silica.

¹H NMR and ¹³C NMR spectra were determined by a Bruker AV400 (400 MHz) NMR spectrometer. The MS spectra were obtained on Nermag France (R10-10C) spectrometer. IR

spectroscopy was performed on Nicolet Avatar 370 MCT using KBr pellets. The melting points of the compounds were determined using an XT-4 microscopic melting point apparatus.

Synthesis of aryl alkynyl substituted carbazole. Typically, Pd(PPh₃)₂Cl₂(200 mg, 0.28 mmol), CuI (1.5 g, 8.0 mmol), PPh₃ (3.14 g, 12.0 mmol) and 3-bromocarbazole (10.0 g, 40.6 mmol) were dissolved in a solution of DMF(100 mL) and TEA(50 mL). The mixture was nitrogen bubbled for 30 min and then slow heated to reflux. *p*-methoxylphenylacetylene was added to the reaction mixture and heated under reflux for 8 hour under nitrogen. Thin-layer chromatography (PE:EA=3:1) was used for monitoring the reaction. The result mixture was filtered to remove salts. The filtrate was concentrated and poured into the saturated NH₄Cl solution and then extracted with CH₂Cl₂. The organic phase was dried and using rotary evaporator to remove the solvent to obtain the Brown dope crude product. The product was purified on a silica gel column using PE/EA(3:1) as eluent and white crystal plate product was obtained.

3-(*p*-Methoxylphenylethynyl)-9H-carbazole(MMoCz). Yield: 70%. m.p.=253-255 °C. ¹H NMR (DMSO-d₆) δ (ppm): 11.49 (s, 1H), 8.35 (s, 1H), 8.19 (d, J = 7.7 Hz, 1H), 7.52-7.50 (m, 5H), 7.43 (t, J = 7.5 Hz, 1H), 7.20 (t, J = 7.4 Hz, 1H), 7.00 (d, J = 8.7 Hz, 2H), 3.81 (s, 3H). ¹³C NMR (100 MHz, DMSO) δ (ppm): 159.12, 140.11, 139.33, 132.60, 128.70, 126.09, 123.49, 122.58, 121.94, 120.55, 119.03, 115.04, 114.35, 112.38, 111.28, 111.15, 89.59, 87.14, 55.21. FT-IR v(cm⁻¹):3402.1 (v, N-H), 2237.0 (v, C≡C), 1178.5 (v, C-N) cm⁻¹. MS m/z: 298.20 (cation+).

3,6-Di(*p*-methoxylphenylethynyl)-9H-carbazole(DMoCz). Yield: 74%. m.p.= 270-273 °C. ¹H NMR (400 MHz, DMSO-d₆) δ (ppm): 11.71 (s, 1H), 8.41 (s, 2H), 7.59 – 7.51 (m, 8H), 7.01 (m, 4H), 3.82 (s, 6H). ¹³C NMR (100 MHz, DMSO) δ (ppm): 159.19, 139.72, 132.65, 129.33, 123.85,

122.15, 114.93, 114.37, 113.01, 111.59, 89.43, 87.42, 55.23. FT-IR ν (cm⁻¹):3398.9 (v, N-H), 2240.4 (v, C≡C), 1187.8 (v, C-N) cm⁻¹. MS m/z: 428.21 (cation⁺).

Synthesis of cationic cyclopentadienylirons of p-methoxylphenyl acetylene carbazole substituted arenes (CzFcs). Typically, an oven-dried three-necked flask was charged with DMF (100 mL), Fc-2Cl (1.8 g, 4.3 mmol), K₂CO₃ (1.2 g, 8.7 mmol) and p-methoxyl phenylethynyl-9H-carbazole (5.4 g, 20 mmol). The reaction mixture was stirred at the 60 °C for 6 hr in darkness until the aryl chloride was completely consumed based on TLC results (acetone/methanol=3:1). The resulting solution was poured into a large amount of water, filtered, and washed with water. All these procedures were operated in darkness. The residue was purified on a silica gel column using acetone as eluent and yellow product was obtained. Other products were synthesized in the same way.

(η^6 -1,4-Bi(9-(3-(p-methoxylphenylethynyl)carbazolyl)) benzene) (η^5 -cyclopentadienyl) iron hexafluorophosphate (MMoCzFc). Yield: 68%. m.p.= 225-228 °C. ¹H NMR (400 MHz, DMSO-d₆) δ (ppm): 8.61 (s, 2H), 8.45 (d, J = 7.1 Hz, 2H), 8.40 (d, J = 8.2 Hz, 2H), 8.05 (d, J = 7.6 Hz, 2H), 7.84 (d, J = 8.2 Hz, 2H), 7.76 (d, J = 7.3 Hz, 2H), 7.67 – 7.41 (m, 8H), 7.15-7.20(m, 2H), 6.95-7.06(m, 4H), 5.38 (s, 5H), 3.84 (s, 6H). ¹³C NMR (100 MHz, DMSO-d₆) δ (ppm): 159.47, 139.39, 138.48, 132.84, 129.94, 127.60, 124.93, 124.06, 123.86, 122.72, 121.36, 116.47, 114.45, 112.05, 111.85, 108.35, 88.89, 88.40, 81.09, 79.70, 78.23, 55.27. FT-IR ν (cm⁻¹):1181.6 (v, C-N), 839.1 (v, PF₆⁻) cm⁻¹. MS: [M -Fe⁺-C₅H₅]⁺790.30.

(η^6 -1,4-Bi(9-(3,6-di((p-methoxylphenyl)ethynyl)-carbazolyl)) benzene) (η^5 -cyclopentadienyl) iron hexafluorophosphate (DMoCzFc). Yield: 71%. m.p.= 235-237 °C. ¹H NMR (400 MHz, DMSO-d₆) δ (ppm): 8.65 (s, 4H), 8.38 (d, J = 8.6 Hz, 4H), 7.86 (d, J = 8.6 Hz, 4H), 7.58 (d, J = 8.5 Hz, 8H), 7.41 (s, 4H), 7.05 (d, J = 8.6 Hz, 8H), 5.39 (s, 5H), 3.84 (s, 12H). ¹³C NMR (100

MHz, DMSO-d₆) δ (ppm): 159.48, 138.72, 132.86, 130.38, 124.25, 124.15, 116.80, 114.42, 112.03, 107.84, 89.04, 88.34, 81.24, 78.48, 55.27. FT-IR ν (cm⁻¹): 1184.7 (v, C-N), 842.2 (v, PF₆⁻) cm⁻¹. MS: [M -Fe⁺-C₅H₅]⁺ 1051.40.

Synthesis of Cz-Ps. The photolysis experiments were conducted in a beaker with a working volume of 100 mL. The reaction beaker was placed in a dark apparatus equipped with a high pressure mercury lamp. Cationic cyclopentadienyliron complexes (1.0g) were dissolved in DMF and the solution surface was 110 mm from the condensation casing of the high pressure mercury lamp. The reaction mixture was irradiated for 30 min with magnetic stirring until the fluorescence spot of cationic cyclopentadienyliron complexes disappeared based on TLC results(acetone/methanol=4:1). After the photolysis, the resulting solution was filtered and the filter cake was purified on a silica gel column (PE:EA=5:1) and light yellow product was obtained. The filtrate was poured into water and the obtained solid was also treated in the same way as the above filter cake. All of the products obtained by the above two steps were target compound.

1,4-Di(9-(3-(4-methoxyphenyl)ethynylcarbazolyl))benzene (MMoCz-P). Yield: 84%. ¹H NMR (400 MHz, DMSO-d₆) δ (ppm): 8.55 (s, 2H), 8.39 (d, J = 7.8 Hz, 2H), 7.98 (s, 4H), 7.73 – 7.60 (m, 6H), 7.60 – 7.50 (m, 6H), 7.40 (t, J = 7.4 Hz, 2H), 7.03 (d, J = 8.8 Hz, 4H), 3.82 (s, 6H). ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 159.44, 141.16, 140.15, 136.54, 132.96, 129.66, 128.42, 126.61, 123.89, 123.67, 123.21, 120.80, 120.65, 115.86, 115.32, 114.04, 109.96, 109.80, 89.03, 87.96, 55.33. FT-IR ν (cm⁻¹): 2225.5 (v, C≡C), 1187.9 (v, C-N) cm⁻¹. MS m/z: 668.90 (cation⁺).

1,4-Di(9-(3,6-di(4-methoxyphenyl)ethynylcarbazolyl))benzene (DMoCz-P). Yield: 85%. ¹H NMR (400 MHz, DMSO-d₆) δ (ppm): 8.61 (s, 4H), 8.01 (s, 4H), 7.68 (m, 8H), 7.56 (d, J = 8.6 Hz, 8H), 7.03 (d, J = 8.7 Hz, 8H), 3.83 (s, 12H). ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 158.47,

139.43, 135.35, 131.96, 129.03, 127.41, 122.97, 122.25, 114.86, 114.71, 113.03, 108.95, 87.78, 87.22, 54.31. FT-IR ν (cm⁻¹): 2203.1 (v, C≡C), 1169.2 (v, C-N) cm⁻¹. MS m/z: 929.36 (cation⁺).

Differential Scanning Calorimetry Measurement Differential scanning calorimetry measurements were carried out under nitrogen atmosphere at a heating rate of 10 °C /min with a Perkin-Elmer TGA Thermal analysis system. The glass transition temperature (T_g) was determined from the second heating scan. Thermal gravimetric analysis was undertaken using a Netzsch STA 449F3 system under nitrogen atmosphere while heating at a rate of 10 °C /min.

Calculation The initial geometry optimization was performed with Gaussview (Version 5.0). For all calculation, Gaussian 09 has been employed. The molecular structures in the ground state were optimized based on density function theory (DFT) at the Becke 3-Lee-Yang-Parr (B3LYP)/Genecp (Fe with Lanl2dz basis set and C, H, N, and O with 6-31G** basic set).

References

- (1) Abd-El-Aziz, A. S.; Schriemer, D. C., The synthesis of new di(cyclopentadienyliron) complexes of polyaromatic ethers. *Inorg. Chim. Acta* **1992**, *202*, 123-125.
- (2) Lu, W.-E.; Dong, X.-Z.; Chen, W.-Q.; Zhao, Z.-S.; Duan, X.-M., Novel photoinitiator with a radical quenching moiety for confining radical diffusion in two-photon induced photopolymerization. *J. Mater. Chem.* **2011**, *21*, 5650-5659.
- (3) Lee, C.-C.; Leung, M.-k.; Lee, P.-Y.; Chiu, T.-L.; Lee, J.-H.; Liu, C.; Chou, P.-T., Synthesis and Properties of Oxygen-Linked N-Phenylcarbazole Dendrimers. *Macromolecules* **2011**, *45*, 751-765.

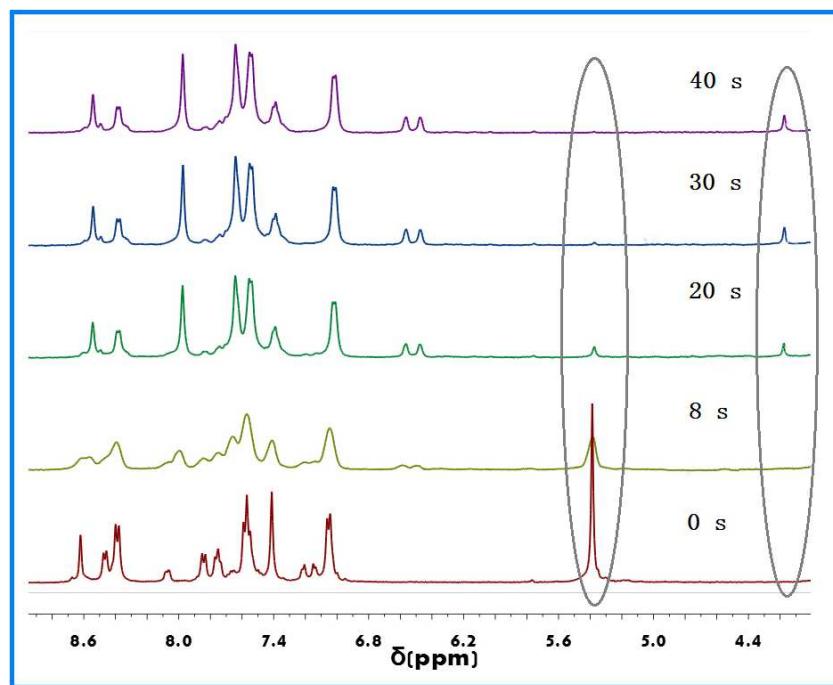


Figure S1. ^1H NMR spectra of MMoCzFc during photolysis under halogen lamp ($\lambda \geq 370\text{nm}$, $\text{DMSO-}d_6$ as the solvents, $M=3.3 \times 10^{-3} \text{ mol/L}$, $I=10\text{mW/cm}^2$)

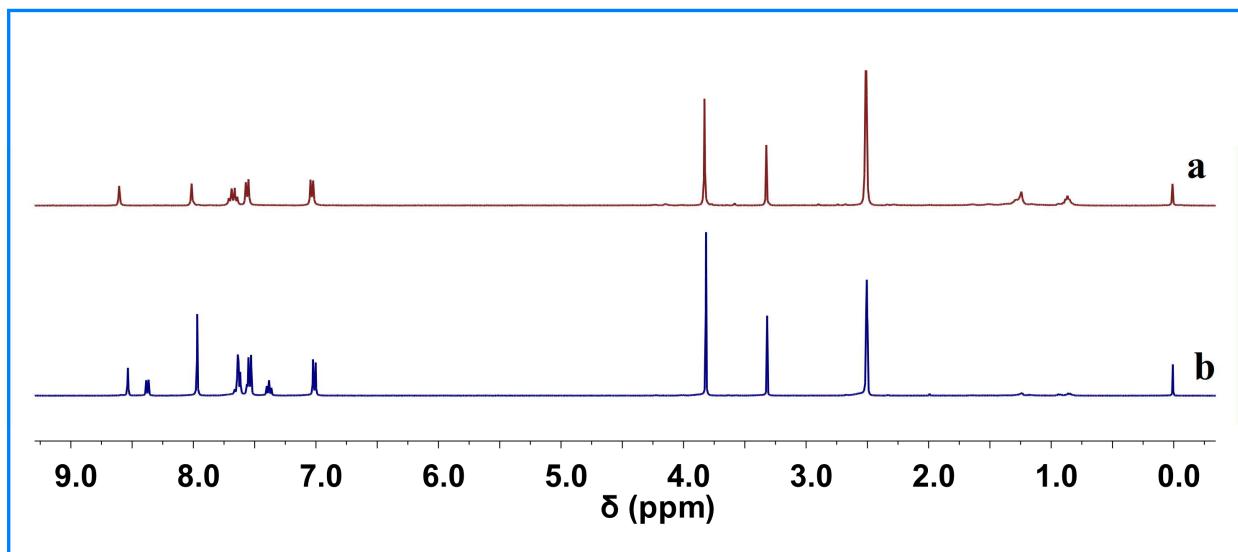


Figure S2. ^1H NMR spectra of Cz-Ps .DMSO- d_6 as the solvents for (a)DMoCz-P and (b)MMoCz-P.

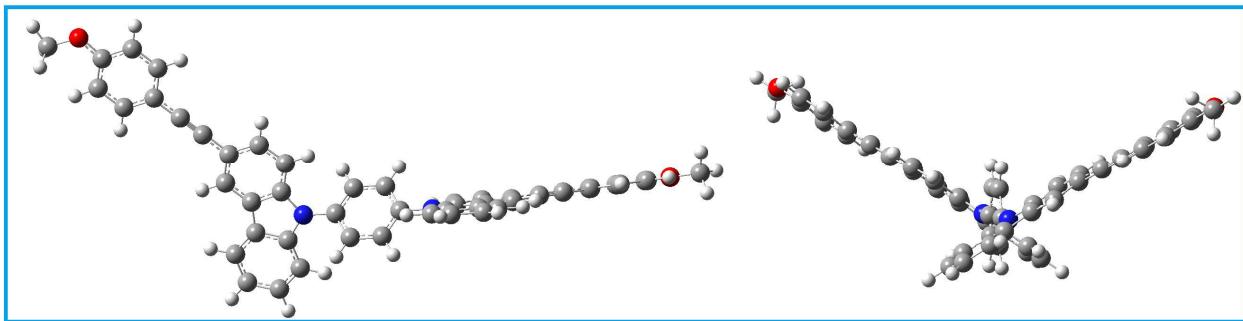
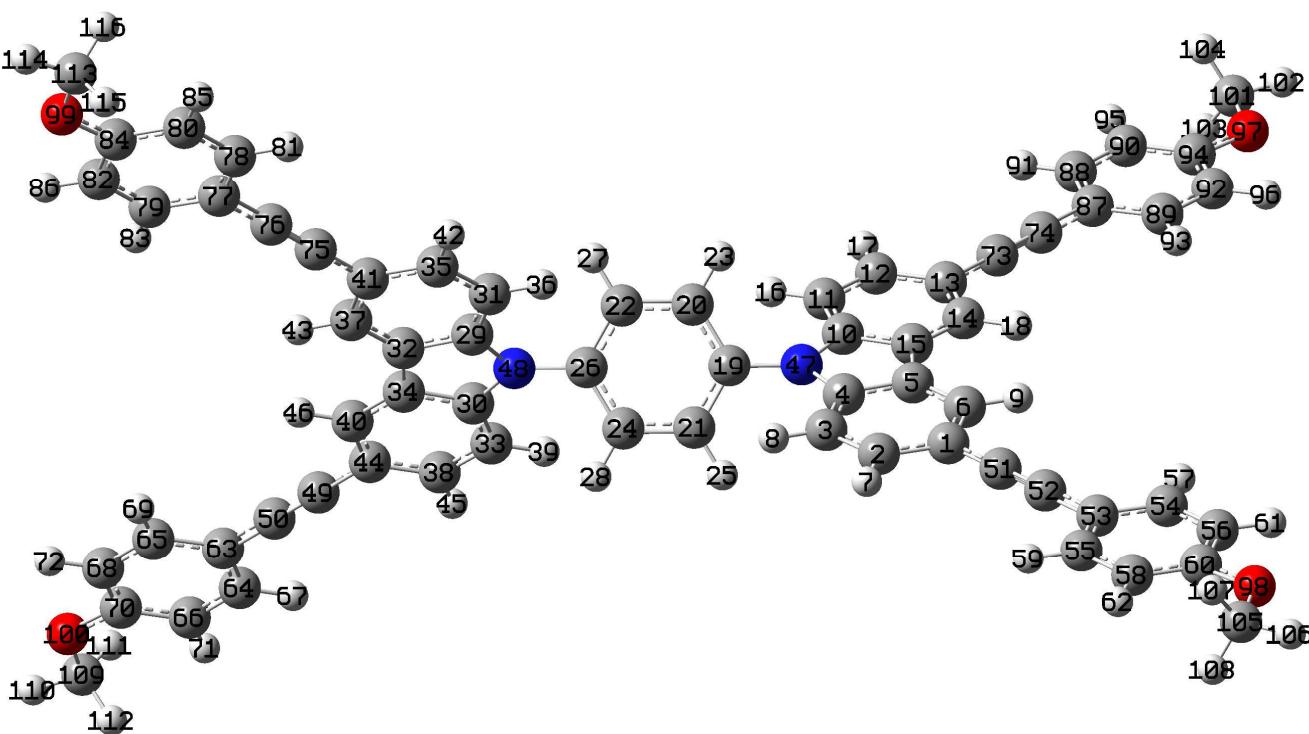


Figure S3. Optimized structures of compound MMoCz-P by DFT method.

Table S1. The optimized structure and part data of selected bond lengths, angles and dihedral angles of DMoCz-P



| Bond lengths(Å) | | Bond angles(°) | | Dihedral angle(°) | |
|-----------------|--------|--------------------|----------|--------------------------|----------|
| O(99)-C(84) | 1.3635 | C(113)-O(99)-C(84) | 118.3444 | C(113)-O(99)-C(84)-C(80) | -0.2531 |
| C(76)-(75) | 1.2171 | C(29)-N(48)-C(26) | 125.7981 | C(31)-C(29)-N(48)-C(26) | -1.8348 |
| N(48)-C(26) | 1.4192 | C(19)-N(47)-C(10) | 125.7979 | C(29)-N(48)-C(26)-C(24) | -55.9935 |
| | | | | C(78)-C(77)-C(41)-C(35) | -0.6126 |

Table S2. The optimized structure and part data of selected bond lengths, angles and dihedral angles of MMoCz-P

Bond lengths(Å)

| | |
|-------------|--------|
| C(76)-O(62) | 1.3638 |
| C(54)-C(53) | 1.2171 |
| N(49)-C(20) | 1.4188 |

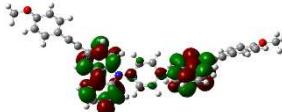
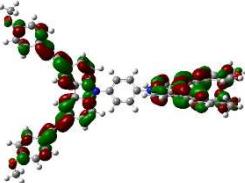
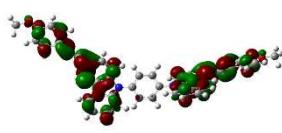
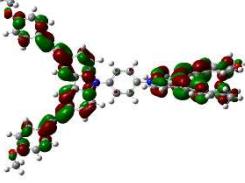
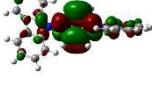
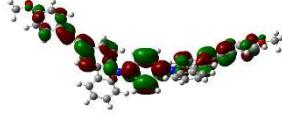
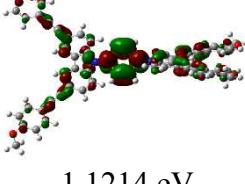
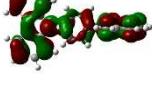
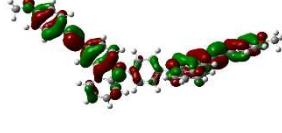
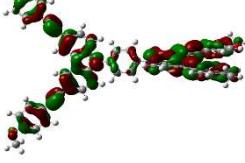
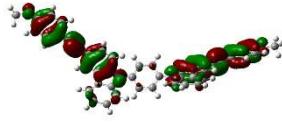
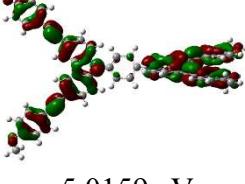
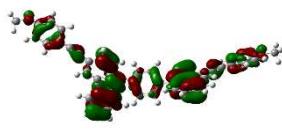
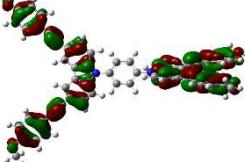
Bond angles(°)

| | |
|-------------------|----------|
| C(77)-O(76)-C(62) | 118.3164 |
| C(20)-N(49)-C(4) | 125.8338 |
| C(27)-N(50)-C(31) | 125.8127 |

Dihedral angle(°)

| | |
|-------------------------|-----------|
| C(77)-O(76)-C(62)-C(58) | 0.0021 |
| C(3)-C(4)-N(49)-C(20) | -1.5918 |
| C(4)-N(49)-C(20)-C(22) | -55.2275 |
| C(57)-C(55)-C(1)-C(6) | -177.3726 |

Table S3. Energy level and electron density distribution of frontier molecular orbitals of Cz-Ps.

| | DCz-P | MMoCz-P | DMoCz-P |
|--------|---|--|---|
| LUMO+2 |  |  |  |
| | -0.7744 eV | -0.8536 eV | -1.0395 eV |
| LUMO+1 |  |  |  |
| | -0.7837 eV | -0.9031 eV | -1.0422 eV |
| LUMO |  |  |  |
| | -0.8136 eV | -1.0544 eV | -1.1214 eV |
| HOMO |  |  |  |
| | -5.3454 eV | -5.0015 eV | -4.9193 eV |
| HOMO-1 |  |  |  |
| | -5.6164 eV | -5.0918 eV | -5.0159 eV |
| HOMO-2 |  |  |  |
| | -5.8303 eV | -5.7533 eV | -5.2918 eV |