Supporting Information for

Construction of a Naphthalimide-Containing Hexagonal Metallocycle *via* Coordination-Driven Self-Assembly and Its Fluorescence Detection of Proton

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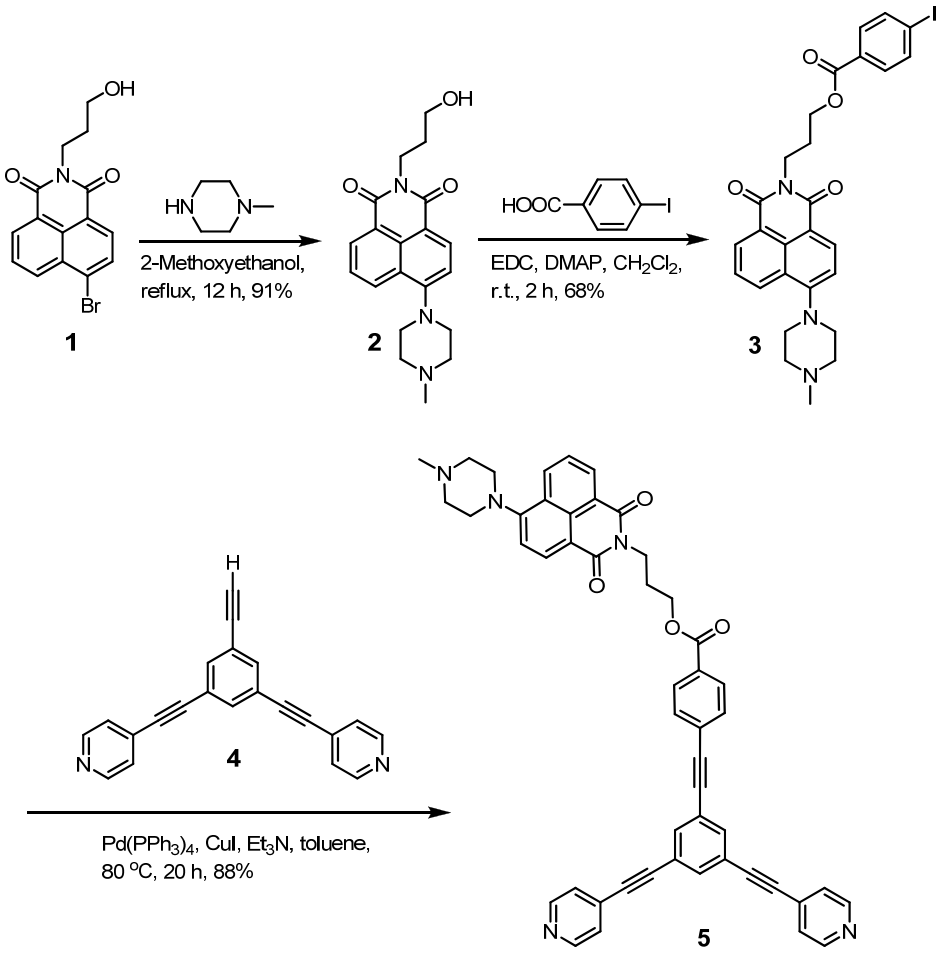
Contents:

Electronic Supplementary Material (ESI) for RSC Advances

1. Synthesis of compounds 2, 3, 4, 5, and 7

General information

Triethylamine (Et_3N), etrahydrofuran (THF) and toluene were dried over potassium hydroxide and all of them were degassed under N_2 for 30 minutes before use. Deuterated solvents were purchased from Cambridge Isotope Laboratory. All other reagents were purchased and used without further purification. NMR spectra were recorded on a Bruker 400 MHz Spectrometer (^1H: 400 MHz; ^{13}C: 100 MHz; ^{31}P: 161.9 MHz) at 298 K. The ^1H and ^{13}C NMR chemical shifts were reported relative to residual solvent signals, and ^{31}P NMR resonances to an internal unlocked sample of 85% H_3PO_4 (δ 0.0). Coupling constants (*J*) were denoted in Hz and chemical shifts (δ) in ppm. Multiplicities are denoted as follows: s = singlet, d = doublet, t = triplet, m = multiplet. UV-Vis spectra were recorded on a Cary 50 Bio UV-vis Spectrophotometer. Emission spectra were measured on a Cary eclipse luminescence spectrometer. Samples for absorption and emission measurements were contained in 1 cm quartz cuvettes.



Scheme S1 Synthesis of naphthalimide-modified 120° di-pyridine donor **5**.

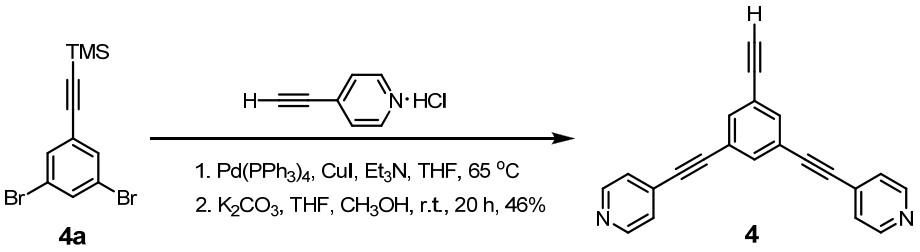
Synthesis of Compound 2

The mixture of compound **1** (1.53 g, 4.58 mmol) and *N*-methyl piperazine (2.54 mL) were dissolved in 2-methoxyethanol (30 mL) and refluxed for 12h. The solvent was removed in vacuo and the crude was purified by column chromatography on silica gel (CH_3OH: CH_2Cl_2 = 20 : 1), affording the yellow solid **2** with the yield of 91%. R_f = 0.36 (CH_3OH: CH_2Cl_2 = 10 : 1, v/v). Mp: 143–144 °C. ^1H NMR ($CDCl_3$, 400 MHz) δ 8.60 (d, *J* = 7.5 Hz, 1H), 8.54 (d, *J* = 8.0 Hz, 1H), 8.41(d, *J* = 8.4 Hz, 1H), 7.71 (t, *J* = 8.4 Hz, 1H), 7.24 (s, 1H), 4.34 (t, *J* = 6.0 Hz, 2H), 3.56 (d, *J* = 4.8 Hz, 2H), 3.38 (s, 4H), 2.86 (s, 4H), 2.51 (s, 3H), 1.98 (t, *J* = 5.2 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 165.17, 164.73, 156.36, 133.07, 131.49, 130.73, 129.96, 126.11, 125.73, 122.87, 116.14, 115.08, 77.48, 77.16, 76.84, 58.87, 55.16, 53.01, 45.18, 36.66, 31.08. IR (neat) ν/cm^{-1}: 3356, 2973, 2883, 1692, 1642, 589, 1454, 1387, 1287, 1235, 1134, 1088, 1048, 1007, 982, 880, 845, 783, 756. ESI-MS calcd for $C_{20}H_{23}N_3O_3Na$: 376.16, found: 376.04. HR-EI-MS calcd for $C_{20}H_{23}N_3O_3$: 353.1739, found: 353.1736.

Synthesis of Compound 3

Compound **2** (1.0g, 2.83 mmol), 4-iodobenzoic acid (0.7 g, 2.83 mmol), EDC·HCl (2.17 g, 11.32 mmol) and DMAP (69 mg, 0.57 mmol) were dissolved in dry CH_2Cl_2 (10 mL), and the reaction mixture was stirred at room temperature for 2 h under argon atmosphere. After that, the reaction solution was washed three times with water, and then the organic phase was dried with Na_2SO_4. After removal of CH_2Cl_2 under reduced pressure, the product was purified by column chromatography on silica gel (CH_3OH: CH_2Cl_2 = 1: 30, v/v), affording the yellow solid **3** with the yield of 68%. R_f = 0.41 (CH_3OH: CH_2Cl_2 = 15 : 1, v/v). Mp: 61°C. ^1H NMR ($CDCl_3$, 400 MHz) δ 8.52 (d, *J* = 7.2 Hz, 1H), 8.45 (d, *J* = 8.0 Hz, 1H), 8.37 (d, *J* = 8.0 Hz, 1H), 7.65 (t, *J* = 8.0 Hz, 1H), 7.56 (s, 4H), 7.19 (d, *J* = 8.0 Hz, 1H), 4.43 (t, *J* = 6.0 Hz, 2H), 3.77 (t. *J* = 6.8 Hz, 2 H), 3.34 (s, 4H), 2.82 (s, 4H), 2.48 (s, 3H), 2.24 (t, *J* = 6.0 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ166.02, 164.62, 164.10, 155.92, 137.46, 132.77, 131.30, 130.97, 130.37, 129.96, 129.69, 126.21, 125.82, 123.21, 116.74, 115.18, 100.55, 63.84, 55.16, 52.85, 46.06, 37.82, 27.36. IR (neat) ν/cm^{-1}: 2940, 2795, 1719, 1694, 1654, 1587, 1514, 1454, 1429, 1393, 1359, 1270, 1236, 1199, 1179, 1140, 1117, 1104, 1068, 1008, 983, 914, 844, 785, 754, 682, 653, 640, 625, 607. ESI-MS calcd for $C_{27}H_{26}IN_3O_4$: 583.108, found: 583.95. HR-EI-MS calcd for $C_{27}H_{26}IN_3O_4$: 583.0968, found: 583.0964.

Synthesis of Compound 4



Scheme S2 Synthesis of compound **4**.

To a 100 mL Schlenk flask, compound **4a** (564.0 mg, 1.7 mmol), 4-ethynylpyridine hydrochloride (715.9 mg, 5.1 mmol), $Pd(PPh_3)_4$ (294.7 mg, 0.225 mmol) and CuI (32.3 mg, 0.17 mmol) were dissolved in a mixed solvent of 15 mL THF and 15 mL Et_3N. The mixture was stirred at 65 °C for 20 h, followed by filtrating insoluble materials and removing the solvent under reduced pressure. The residue was general purified by column chromatography on silica gel (CH_3COCH_3: CH_2Cl_2 = 1 : 10, v/v), affording the white crude. Then the crude was dissolved into a mixture of isovolumetric THF and methanol with K_2CO_3 for 2h. The solid was again filtrated and the remaining solvent was removed,

followed by the purification on silica gel column chromatography (CH_3COCH_3: CH_2Cl_2 = 1 : 10, v/v), affording the white solid **4** with the yield of 46%. R_f = 0.24 (CH_3COCH_3: CH_2Cl_2 = 1 : 5, v/v). Mp: 131–132 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.63 (d, *J* = 8.0 Hz, 4H), 7.71 (s, 1H), 7.67 (s, 2H), 7.39 (d, *J* = 5.6Hz, 4H), 3.17 (s, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 150.03, 135.69, 135.10, 130.84, 125.68, 123.51, 123.29, 91.70, 88.17, 81.55, 79.28. IR (neat) *v*/cm^{-1}: 3295, 3042, 2214, 1594, 1538, 1406, 1215, 991, 968, 883, 816, 788, 746, 678, 660, 615. EI-MS calcd for $C_{22}H_{12}N_2$: 304, found: 304. HR-EI-MS calcd for $C_{22}H_{12}N_2$: 304.1000, found: 304.0999.

Synthesis of compound 5

To a 50 mL Schlenk flask, compound **3** (100 mg, 0.17 mmol), **4** (52.16 mg, 0.17 mmol), $Pd(PPh_3)_4$ (30 mg, 0.026 mmol) and CuI (3.2 mg, 0.017 mmol) were dissolved in a mixed solvent of 10 mL toluene and 10 mL Et_3N. The mixture was stirred at 80 °C for 20 h, followed by filtrating insoluble materials and removing the solvent under reduced pressure. The residue was purified by column chromatography on silica gel (CH_3OH: CH_2Cl_2 = 1 : 20, v/v), affording the yellow solid **5** with the yield of 88%. R_f = 0.41 (CH_3OH: CH_2Cl_2 = 1 : 10, v/v). Mp: 107–108 °C. ^{1}H NMR(CD_2Cl_2, 400 MHz) δ 8.63-8.61 (m, 4H), 8.8.41 (t, *J* = 8.0 Hz, 2H), 7.85 (d, *J* = 8.4 Hz, 2H), 7.76 (s, 3H), 7.69 (t, *J* = 8.4 Hz, 1H), 7.43–7.42 (m, 4H), 7.41 (s, 1H), 7.39 (s, 1H), 7.20 (d, *J* = 8.0 Hz, 1H), 4.43 (t, *J* = 6.0 Hz, 2H), 4.37 (t, *J* = 6.8 Hz, 2H), 3.34 (s, 4H), 2.76 (s, 4H), 2.41 (s, 3H), 2.24 (t, *J* = 6.4 Hz, 2 H). ^{13}C NMR (CD_2Cl_2, 100 MHz): δ.165.84, 164.59, 164.08, 155.84, 150.03, 135.21, 134.85, 132.74, 131.50, 131.30, 130.79, 130.34, 130.21, 129.96, 129.61, 126.85, 126.22, 125.84, 125.64, 124.12, 123.36, 123.23, 116.83, 15.23, 91.74, 90.59, 89.86, 88.21, 63.73, 55.12, 52.74, 45.96, 37.76, 29.80, 27.45. IR (neat) ν/cm^{-1}: 1718, 1694, 1655, 1592, 1538, 1514, 1455, 1395, 1357, 1271, 1236, 1181, 1139, 1108, 1092, 1066, 1007, 990, 966, 880, 860, 820, 785, 768, 760, 737, 694, 679, 643, 629, 611. ESI-MS calcd for $C_{49}H_{37}N_5O_4$: 759.28, found: 760.15.

Synthesis of compound 7

The mixture of 120° di-Pt (II) acceptor **6** (6.57 mg, 0.00490 mmol) and compound **5** (3.72 mg, 0.00490 mmol) was dissolved in 2 mL dichloromethane and stirred for 12 h at room temperature. The solution was evaporated to dryness to give the product **7** in the yield of 97%. ^{1}H NMR (CD_2Cl_2, 400 MHz): δ8.73 (m, 12 H), 7.49 (d, *J* = 6.0 Hz, 4H), 8.427 (d, *J* = 8.4 Hz, 6H), 8.00 (s, 3H), 7.927.83 (m, 24 H), 7.69 (t, *J* = 8.0 Hz, 4 H), 7.57–7.52 (m, 24H), 7.46 (d, *J* = 8.2 Hz, 8H), 8.20 (d, *J* =8.0 Hz, 4H), 4.39 (s, 6H), 4.4.36 (d, *J* = 6.8 Hz, 6H), 3.30 (s, 12H), 2.71 (s, 12H), 2.37 (s, 9H), 2.24 (t, *J* = 6.4 Hz, 6H), 1.37 (br, 72H), 1.19–1.13 (m, 108H). ^{31}P NMR (CD_2Cl_2, 161.9 Hz): δ 13.52 (s, $^{1}J_{Pt\text{-}P}$ = 2655.9 Hz). IR (neat) ν/cm^{-1}: 2966, 1717, 1694, 1654, 1608, 1577, 1536, 1455, 1418, 1392, 1357, 1306, 1267, 1224, 1176, 1151, 1106, 1066, 1031, 1007, 926, 881, 841, 787, 761, 735, 698, 676, 637. CSI-TOF-MS for $[M\text{-}4OTf]^{4+}$: 1426.8. Anal. Calcd for : $C_{264}H_{315}F_{18}N_{15}O_{33}P_{12}Pt_6S_6 \cdot 0.5\ CH_2Cl_2$： C, 50.07; H, 5.02; N, 3.31. Found: C, 49.86; H, 5.31; N, 3.40.

2. ^{1}H NMR, ^{13}C NMR or ^{31}P NMR spectrum of 2, 3, 4, 5, and 7

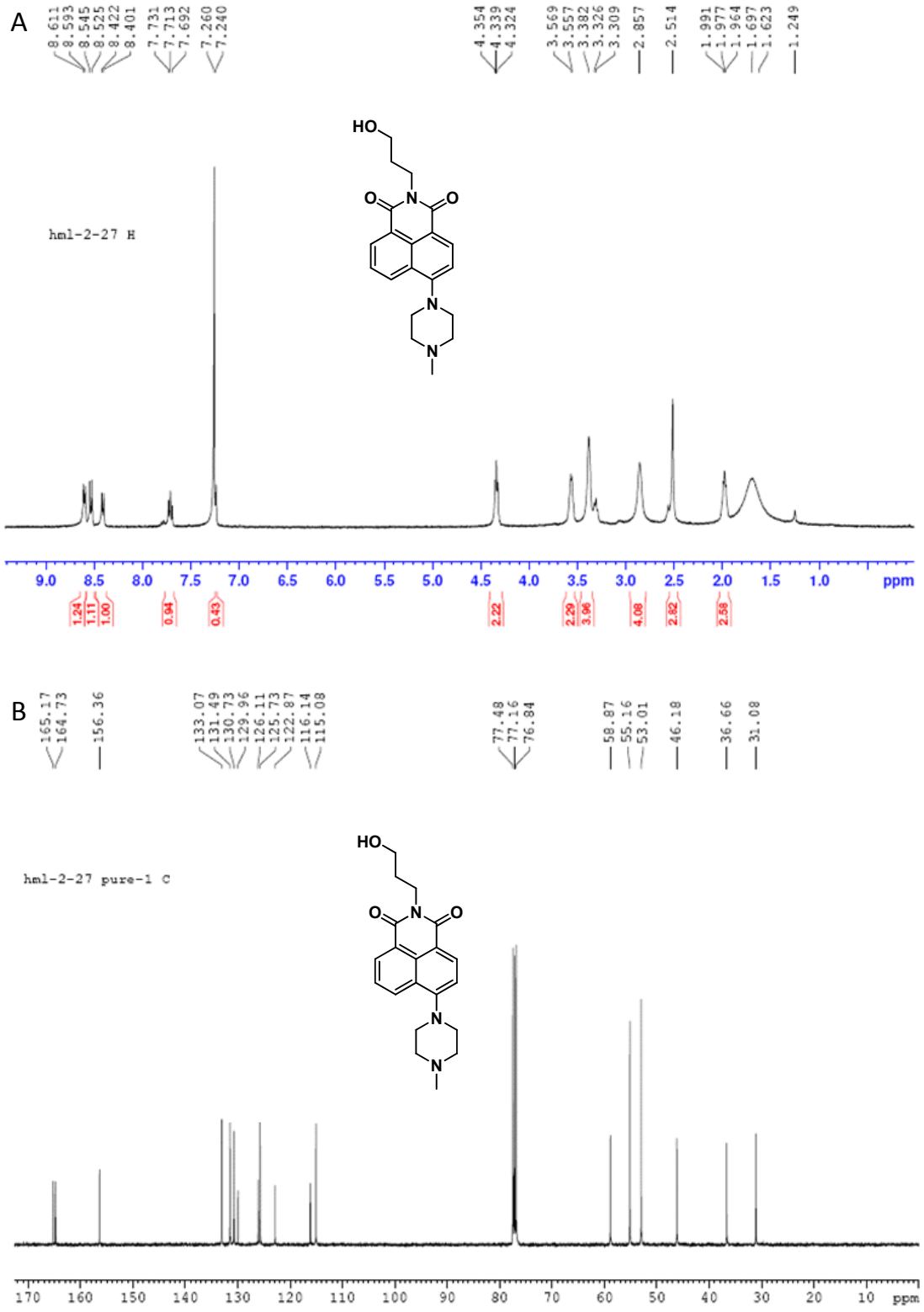


Fig. S1 ^{1}H NMR (A) and ^{13}C NMR (B) spectra of **2** in $CDCl_3$.

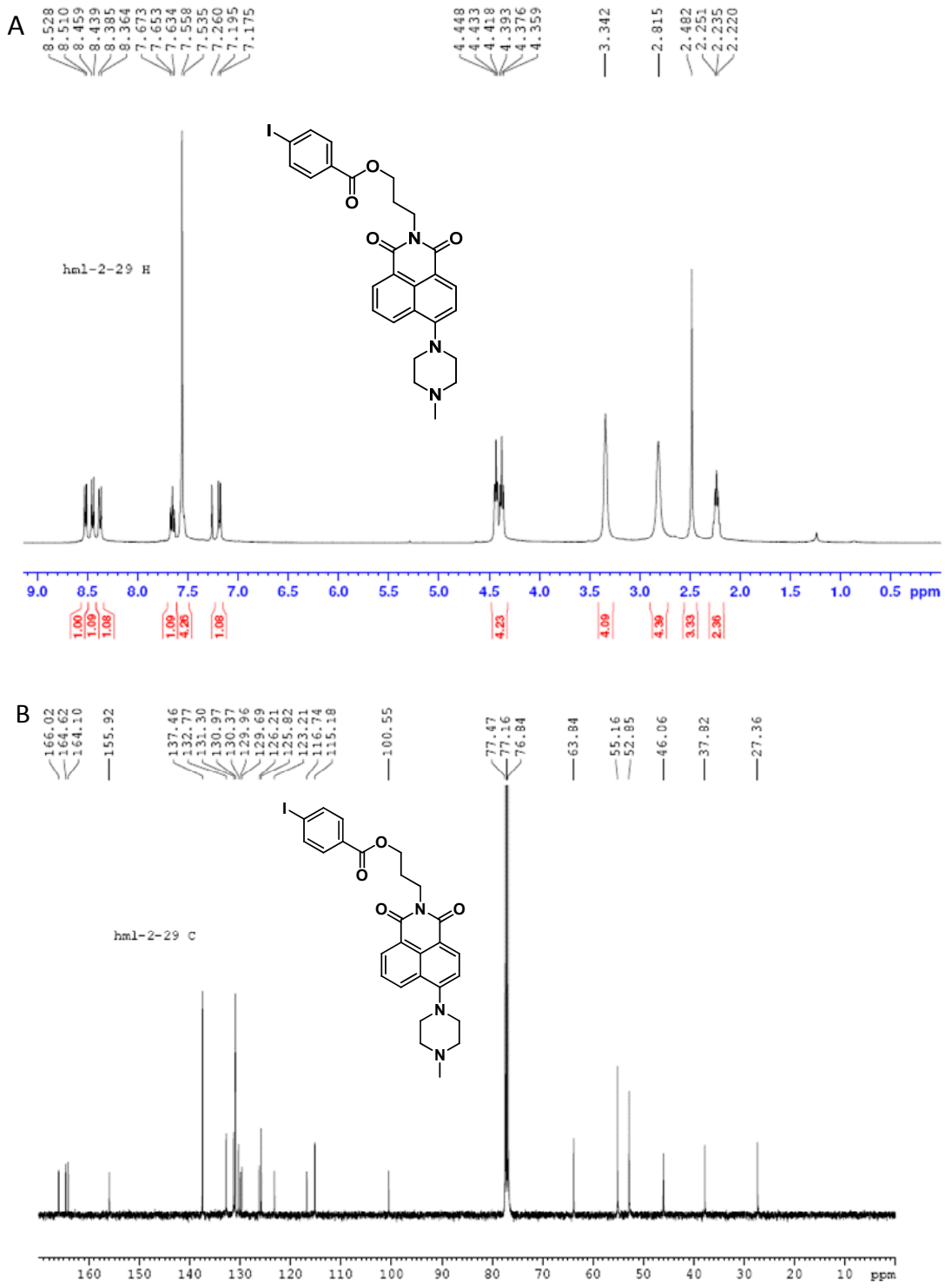


Fig. S2 ^{1}H NMR (A) and ^{13}C NMR (B) spectra of **3** in $CDCl_3$.

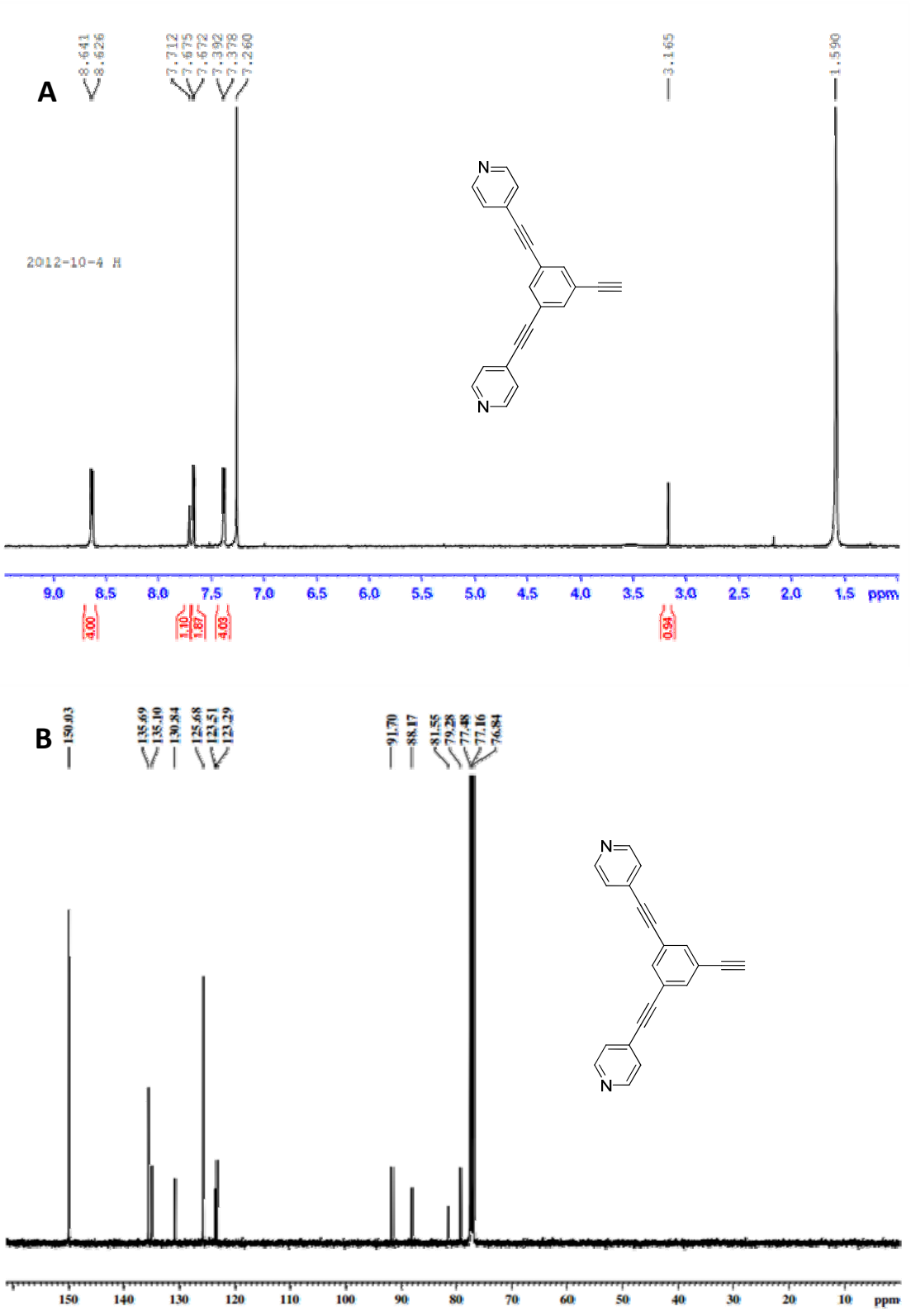


Fig. S3 ^{1}H NMR (A) and ^{13}C NMR (B) spectra of **4** in $CDCl_3$.

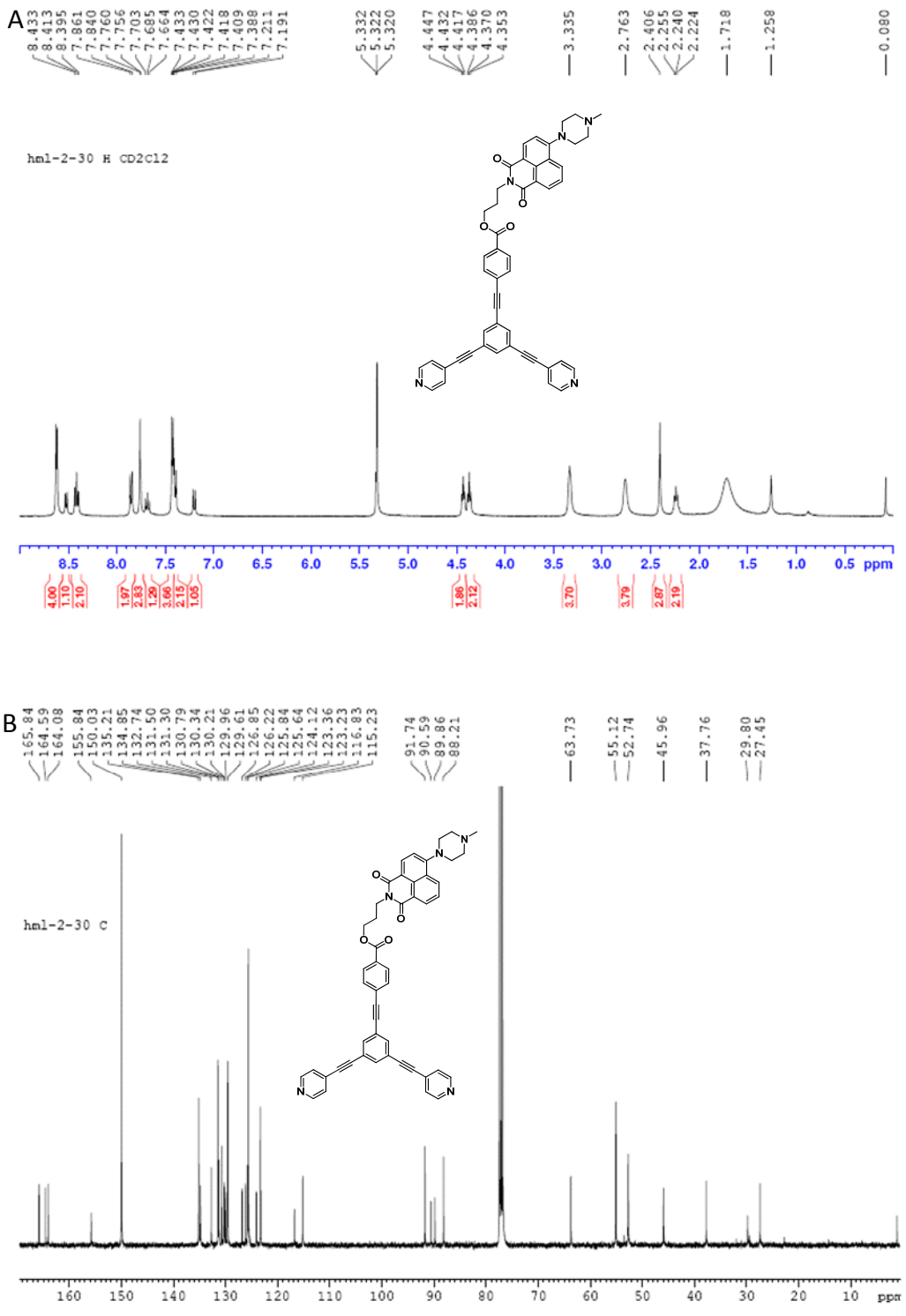


Fig. S4 ^{1}H NMR (A) and ^{13}C NMR (B) spectra of **5** in CD_2Cl_2 and in $CDCl_3$, respectively.

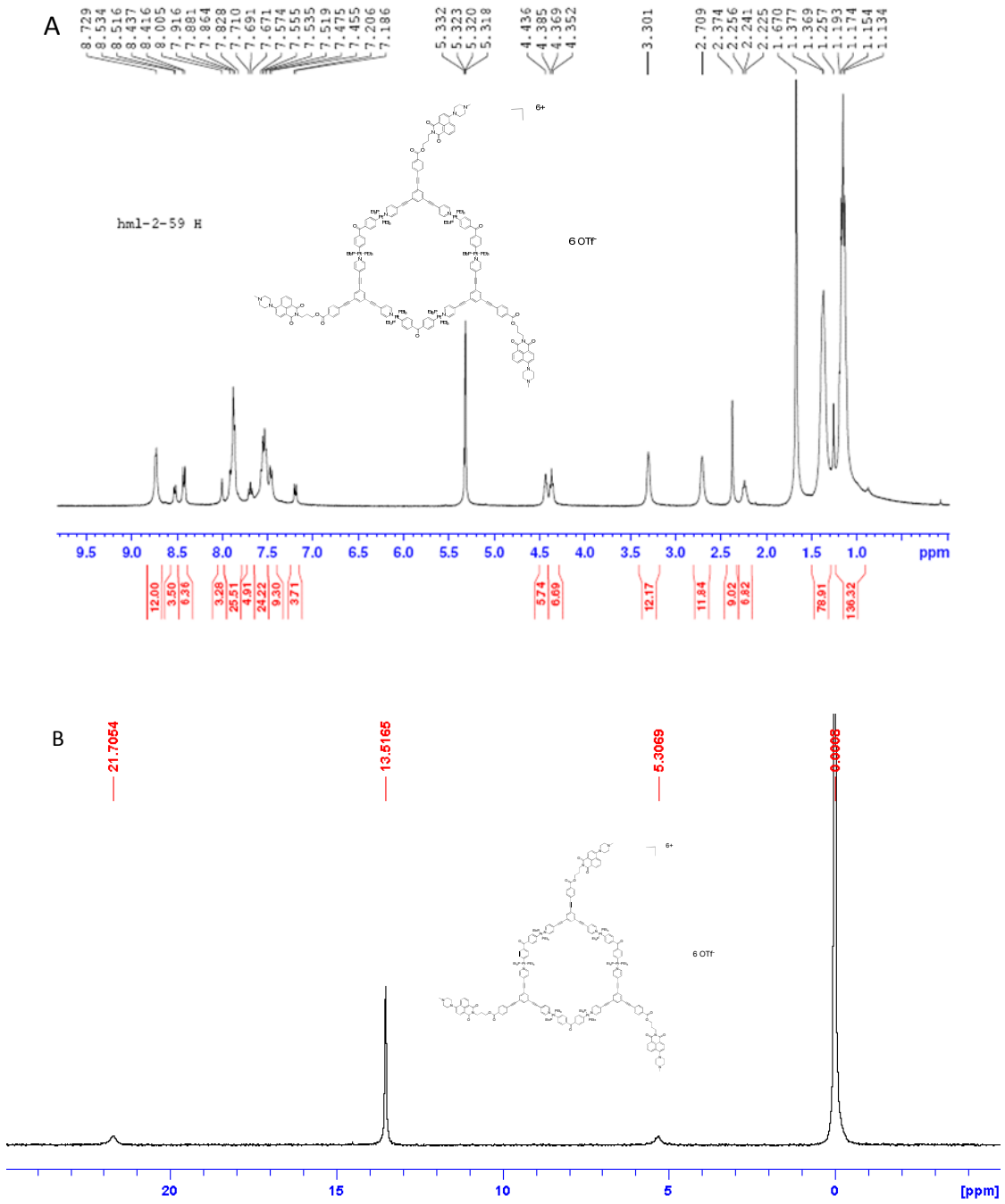


Fig. S5 ^{1}H NMR (A) and ^{31}P NMR (B) spectra of **7** in CD_2Cl_2.

3. Partial ^{1}H NMR spectra of 5 and 7

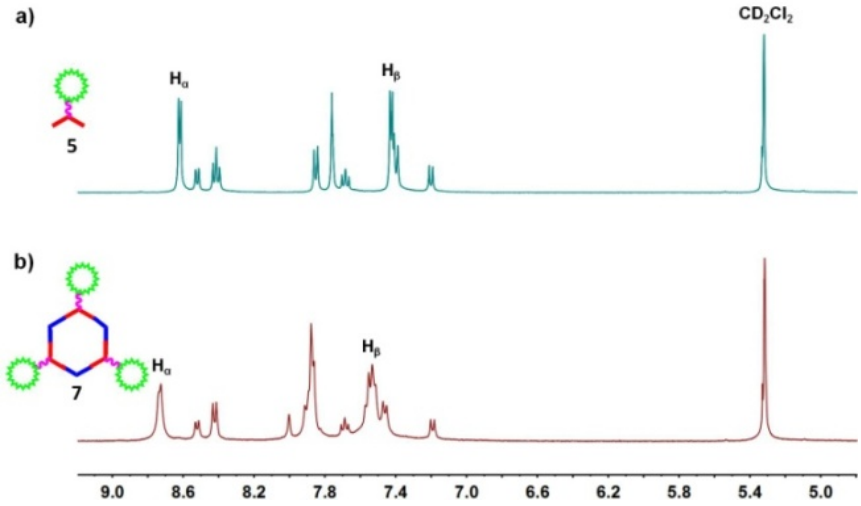


Fig. S6 Partial ^{1}H NMR spectra of 120^{o} di-pyridine donor **5** (a) and hexagonal metallocycle **7** (b).

4. ^{1}H and ^{31}P NMR spectrum of metallocycle 7 with and without 3 equivalent CF_3COOD

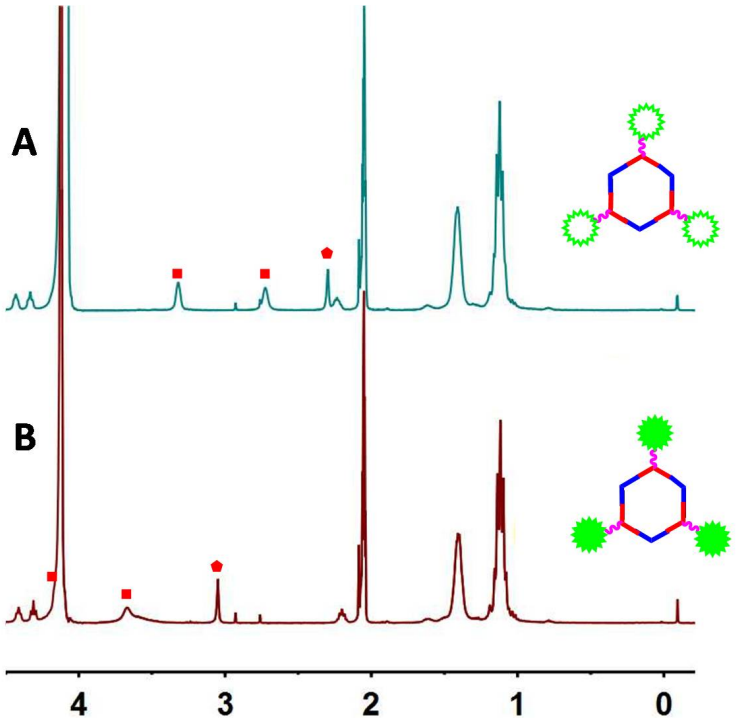


Fig. S7 Partial ^{1}H NMR of compound **7** without (A) and with (B) 3 equivalent of CF3COOD. ⬟ represent hydrogen atoms on methyl group of N-methyl piperazine; ■ represent hydrogen atoms on piperazine ring of N-methyl piperazine.

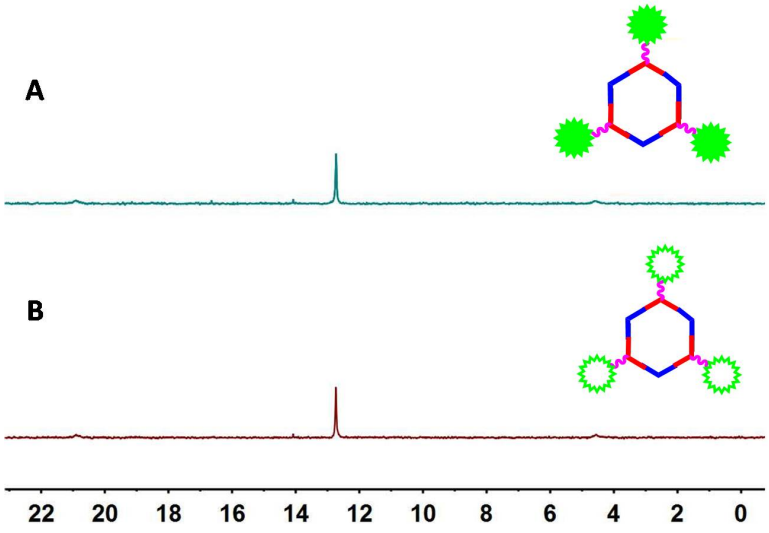


Fig. S8 ^{31}P NMR of compound **7** with (A) and without (B) 3 equivalent of CF_3COOD.

5. UV-Vis absorption spectra of 5 and 7

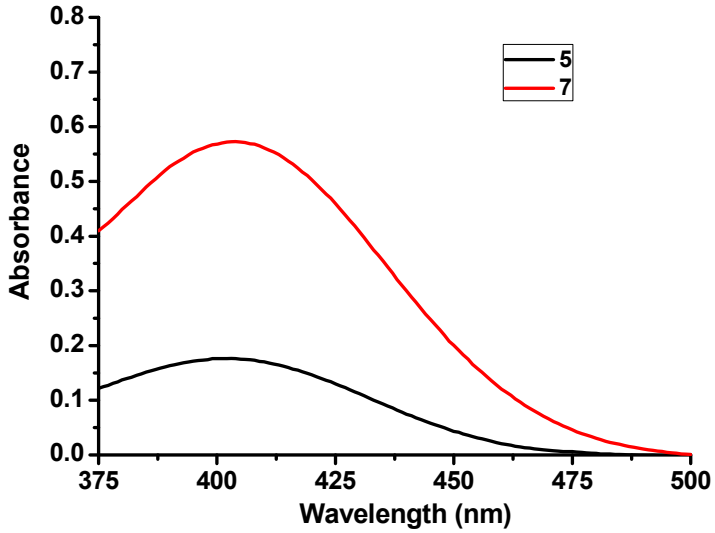


Fig. S9 UV-Vis absorption spectra of **5** (20 μM) and **7** (20 μM) in aqueous solution (acetone/water, 4/1, v/v).

6. Fluorescence intensity of 7 versus pH

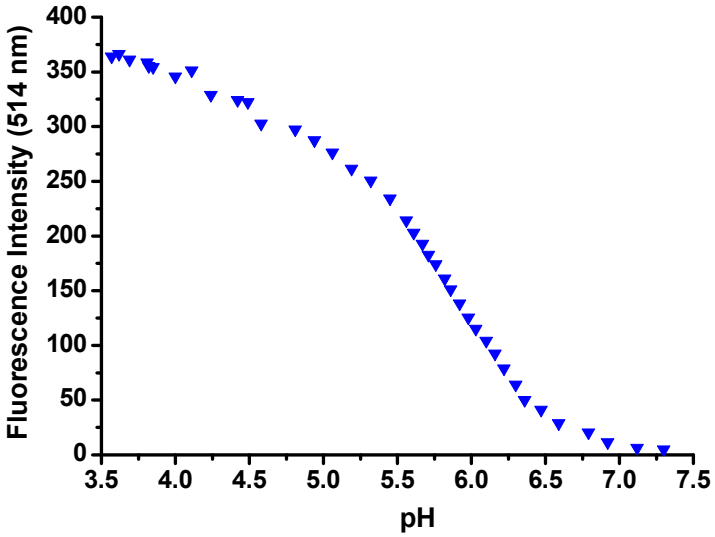


Fig. S10 Fluorescence intensity at 514 nm of **7** versus pH according to the fluorescent pH titration.

7. Fluorescence response of 5 to proton

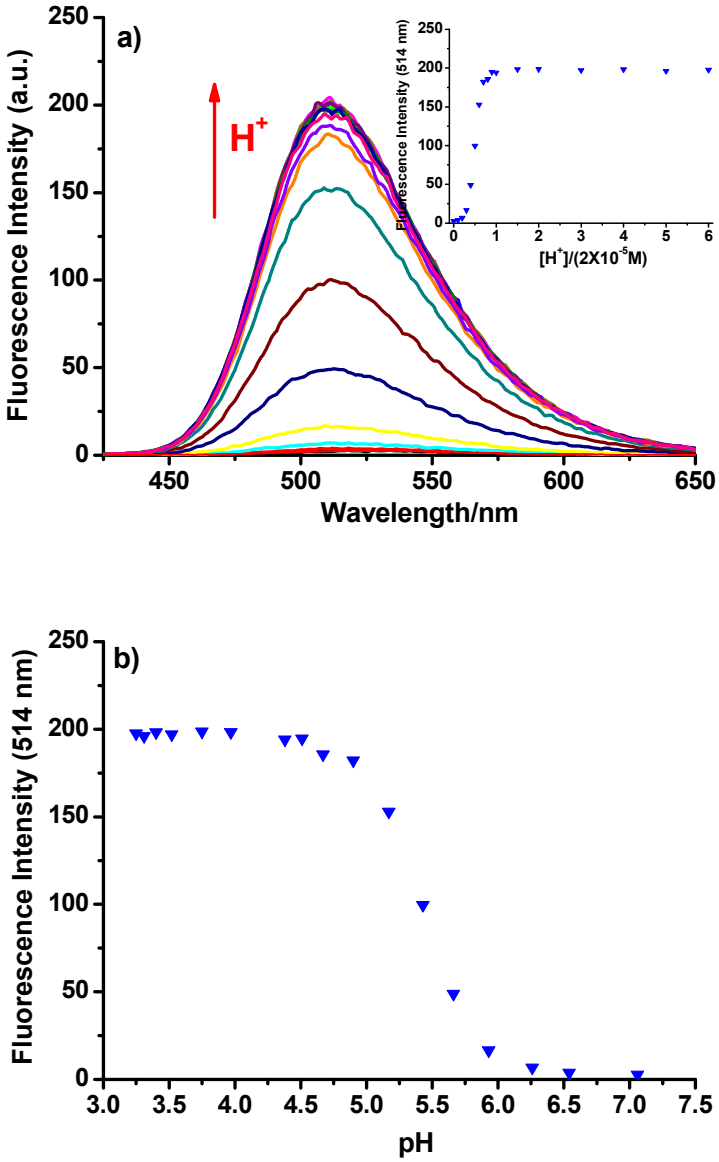


Fig. S11 Fluorescence spectra of **5** (a, 20 μM) upon addition of proton in aqueous solution (acetone/water, 4/1, v/v); fluorescence intensity at 514 nm of **5** (b) versus pH according to the fluorescent pH titration. Inset: Curve of fluorescence intensity at 514 nm of **5** versus increasing concentrations of CF_3COOH.

8. Fluorescence response of 7 to proton and base

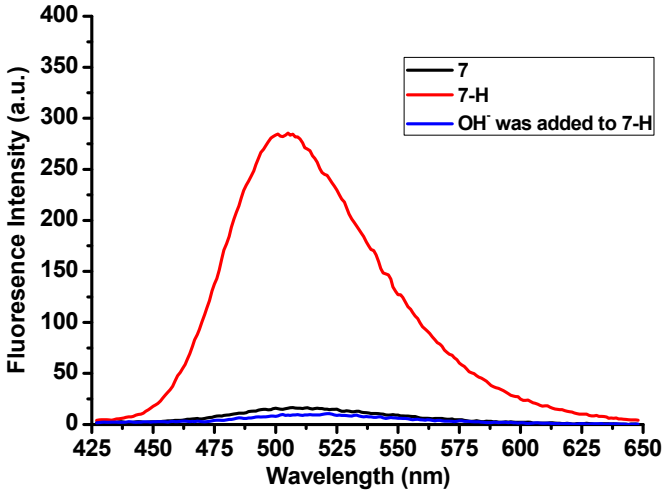


Fig. S12 Fluorescence spectra of **7** (20 μM) upon addition of 3 equiv. proton and then 3 equiv. base in aqueous solution (acetone/water, 4/1, v/v).