

## Supporting information

### Experimental

All solvents and chemicals were purchased from commercial sources and used without further purification unless otherwise stated. 1,1,2,2-tetrakis(4-fluorophenyl)ethylene was synthesized according to the published procedure.<sup>[1]</sup>  $^{13}\text{C}\{^1\text{H}\}$  and  $^{31}\text{P}\{^1\text{H}\}$  cross polarized magic angle spinning nuclear magnetic resonance (CP/MAS NMR) spectra were recorded using a 400 MHz WB Solid-State NMR Spectrometer superconducting nuclear magnetic resonance spectroscopy instrument. Thermo analyses were performed under an  $\text{N}_2$  atmosphere at a heating rate of  $10^\circ\text{C min}^{-1}$  with a NETZSCH TG 209F3 system. X-ray powder diffraction data were collected on a Bruker D8 ADVANCE diffractometer at 40 kV and 40 mA with a Cu-target tube and a graphite monochromator ( $\lambda = 1.5418 \text{ \AA}$ ). UV-vis absorption and luminescence spectra were recorded on a UV-3150 UV-vis spectrophotometer (Shimadzu) and a FLS920 Combined Lifetime and Steady State Fluorometer (Edinburgh Instruments Ltd.), respectively.

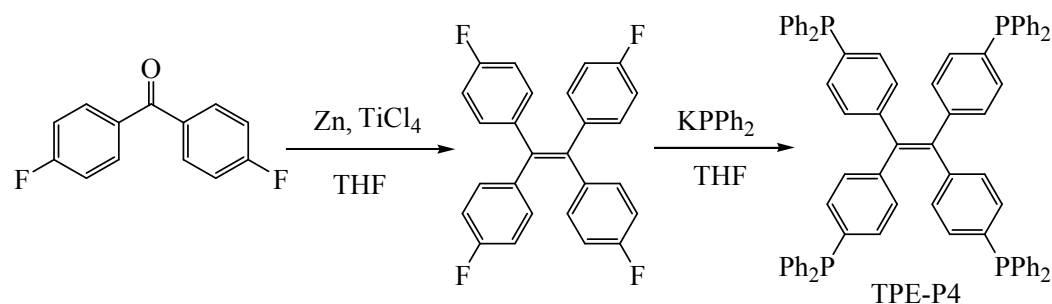
Synthesis of 1,1,2,2-tetrakis((4-diphenylphosphino)phenyl)ethylene (TPE-P4). The reaction was performed under pure dry nitrogen using standard Schlenk techniques. To 1,1,2,2-tetrakis(4-fluorophenyl)ethylene (303.3 mg, 0.75 mmol) in THF (30 mL, distilled from K under nitrogen) was added dropwise  $\text{KPPH}_2$  (6.0 mL,  $0.5 \text{ mol L}^{-1}$  in THF, 3.00 mmol) with stirring. The reaction mixture was stirred for 30 min at RT and then was brought to reflux for 5 h. THF was removed under reduced pressure and MeOH (3 mL) was added to the residue. The white solid was collected by filtration and washed with EtOH ( $10 \text{ mL} \times 3$ ). Yield: 0.272 g, 34%.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta = 7.68\text{--}7.07$  (m, 18H),  $7.07\text{--}6.85$  (m, 4H), 3.52 (s, 1H), 1.59 (s, 24H), 1.28 (s, 8H), 0.10 (s, 2H), 0.02 ppm (d,  $J = 3.2 \text{ Hz}$ , 8H).  $^{31}\text{P}\{^1\text{H}\}$  NMR (162 MHz,  $\text{CDCl}_3$ )  $\delta = -6.1$  ppm (s). MS (EI):  $m/z$  (%): 1069.1 ( $[M^+]$ ).

Synthesis of  $[\text{Ag}_2(\text{TPE-P4})\text{CO}_3]_x \cdot n\text{H}_2\text{O}$  (Ag-TPE-P4). A solution of  $\text{AgBF}_4$  (0.94 mg,

0.005 mmol) in acetonitrile (1.0 mL) was added dropwise to a solution of TPE-P4 (2.7 mg, 0.0025 mmol) in toluene (1.0 mL). The reaction mixture was stirred protected from light for 10 min. The resulting yellow solution was kept in a closed vial at 80°C. Yellow rod crystals suitable for single-crystal X-ray diffraction analysis were obtained after 2 d (1.6 mg, 46%). Found (calcd.) for  $C_{79}H_{66}P_4Ag_2O_4B_2F_8N_2$ : C 58.90 (58.55), H 4.38 (4.10), N 1.85 (1.73)%.  $^{13}C\{^1H\}$  CP NMR (101 MHz)  $\delta = 194.9, 148.8\text{--}135.3, 119.6$  ppm.  $^{31}P\{^1H\}$  CP NMR (162 MHz)  $\delta = 13.2$  (br) ppm. IR (KBr): 1633 (s), 1600 (w), 1480 (m), 1433 (m), 1382 (m), 1339 (w), 1162 (m), 1096 (s), 1065 (w), 1031 (w), 744 (s), 694 (s), 661 (m), 543 (m),  $491\text{ cm}^{-1}$  (m).

X-ray crystallography. X-ray crystallographic data of Ag-TPE-P4 were collected at 150(2) K on an Agilent SuperNova X-ray diffractometer system equipped with CCD detector using Cu X-ray tube. The structure was solved by the direct method following difference Fourier syntheses, and refined by the full-matrix least-squares method against  $F_0^2$  using SHELXTL software. All non-hydrogen atoms were refined with anisotropic thermal parameters while hydrogen atoms were introduced in the final refinement model in calculated positions with isotropic thermal parameters. The disordered solvated molecules could not be exactly determined and the hydrogen atoms of solvated water molecules were not added. Selected bond lengths and bond angles are given in Table S2.

[1] Z. Huang, C. Velázquez, K. Abdellatif, M. Chowdhury, S. Jain, J. Reisz, J. DuMond, S. B. King, E. Knaus, *Org. Biomol. Chem.* **2010**, *8*, 4124-4130.



Scheme S1. Synthetic route for TPE-P4.

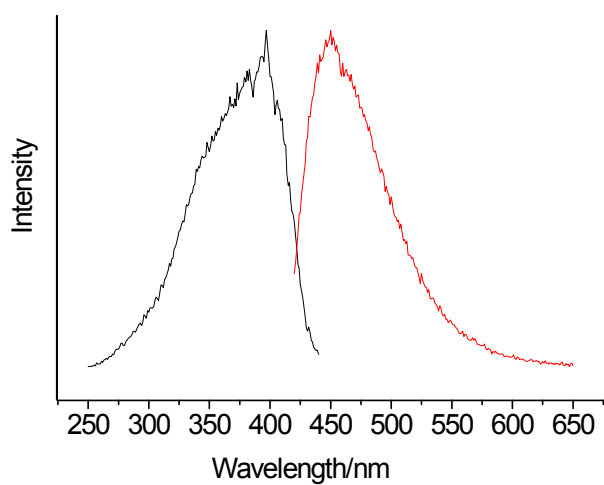


Figure S1. Solid-state excitation and emission photoluminescence spectra of TPE-P4 (as-synthesized) measured at room temperature ( $\lambda_{\text{ex}} = 397 \text{ nm}$ ,  $\lambda_{\text{em}} = 450 \text{ nm}$ ).

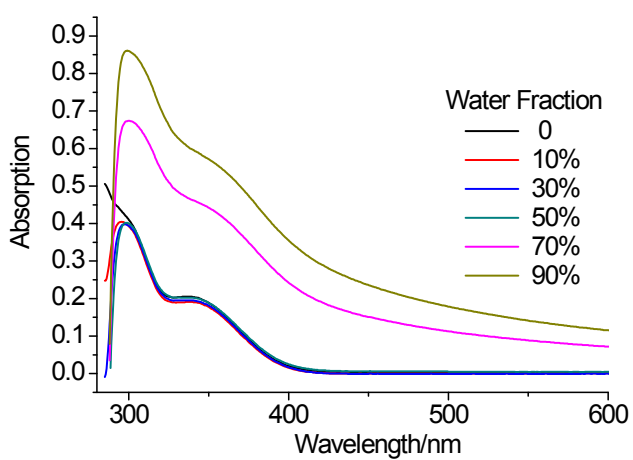


Figure S2. UV-vis absorption spectra of TPE-P4 in THF-water mixtures with different water fractions ( $c = 10^{-5} \text{ mol L}^{-1}$ ).

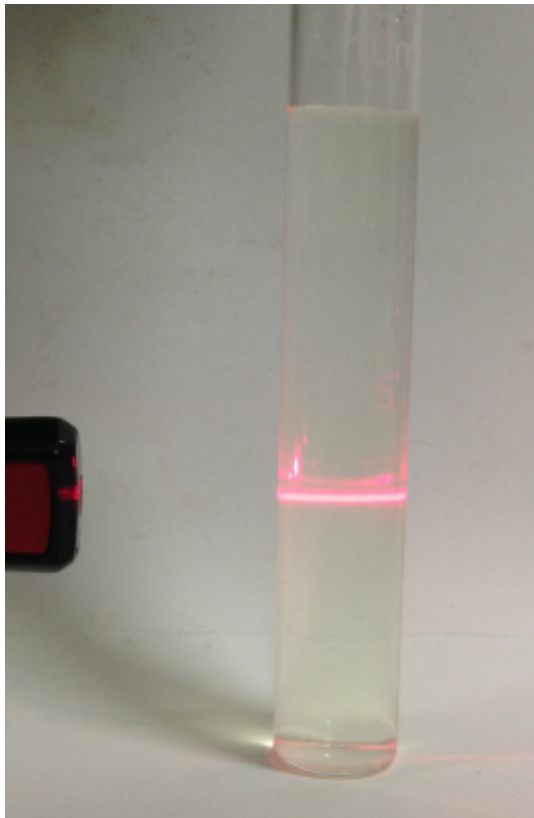


Figure S3. The Tyndall effect of TPE-P4 with water fraction 90% in THF/water mixture ( $c = 10^{-5} \text{ mol L}^{-1}$ ).

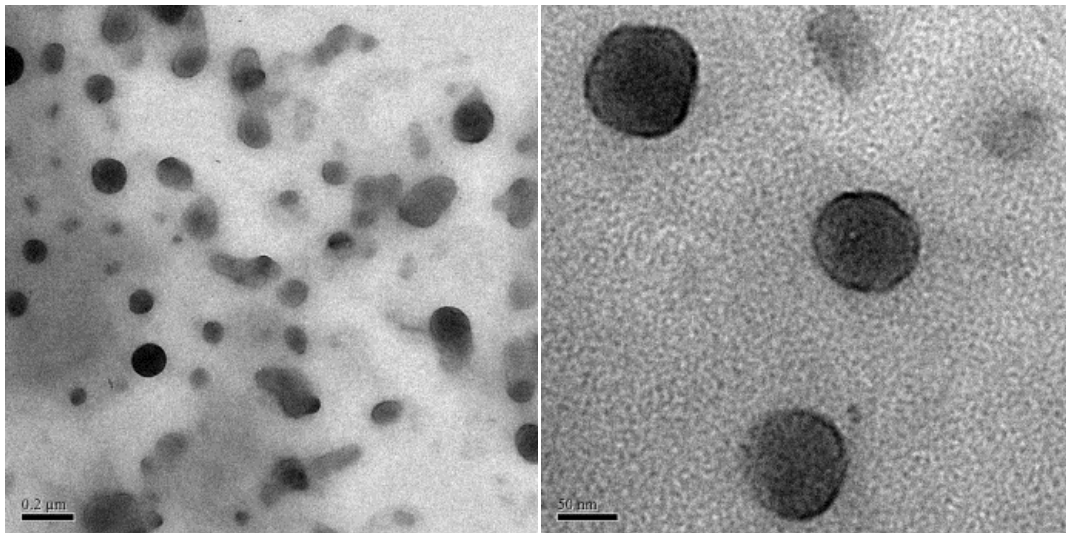


Figure S4. TEM images of TPE-P4 with water fraction 90% in THF/water mixture ( $c = 10^{-5} \text{ mol L}^{-1}$ ).

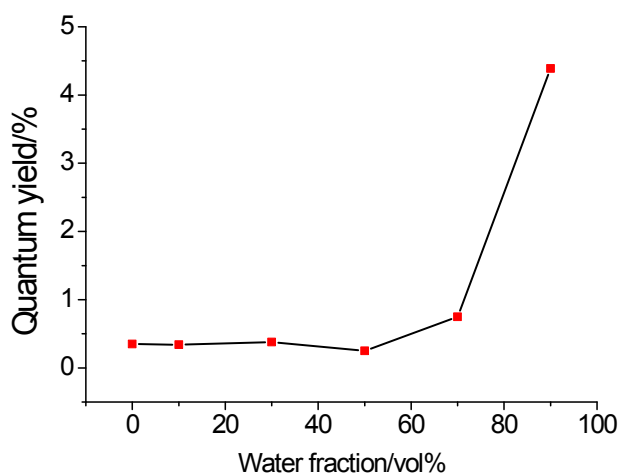


Figure S5. Variations of fluorescence quantum yields of TPE-P4 with water fractions in THF/water mixtures ( $c = 10^{-5}$  mol L $^{-1}$ ;  $\lambda_{\text{ex}} = 350, 365$  and  $375$  nm) using 9,10-diphenylanthracene ( $\Phi = 95\%$  in EtOH) as standard.

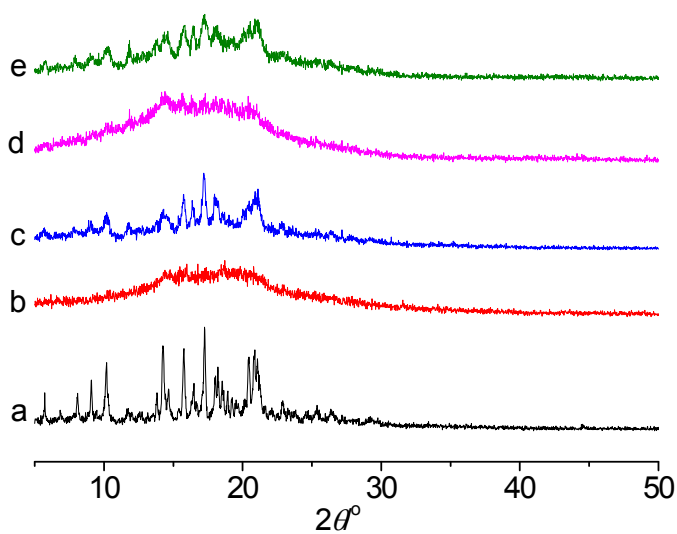


Figure S6. XRPD patterns of TPE-P4, a) as-synthesized sample, b) ground sample, c) sample exposed to MeOH vapor, d) re-ground sample, and d) sample re-exposed to MeOH vapor.

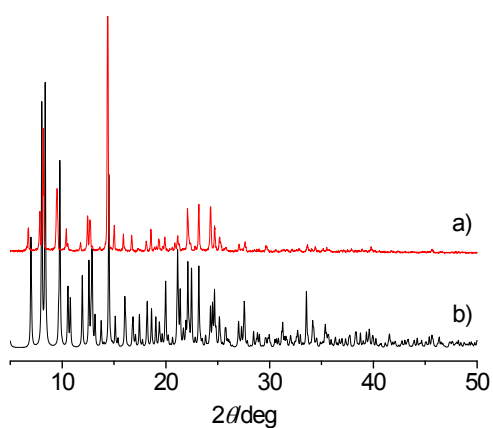


Figure S7. XRPD patterns of Ag-TPE-P4, a) as-synthesized, b) simulated from the CIF file. The slight shift of all the peaks may be attributed to the temperature effect (Single-crystal X-ray data was collected at 150 K and the PXRD data of as-synthesized material was collected at RT).

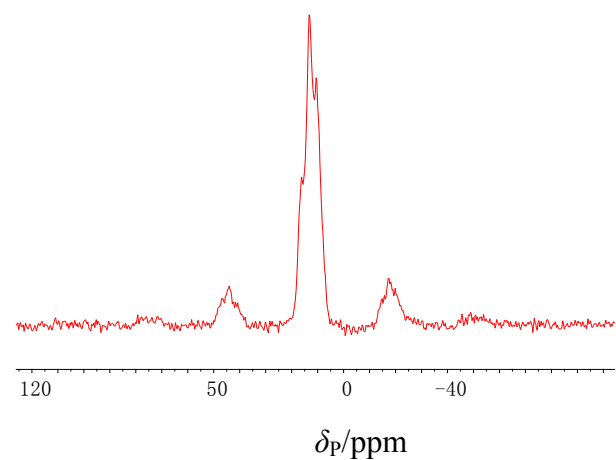
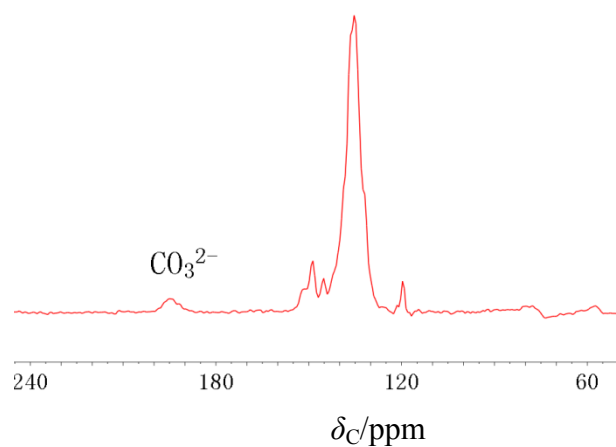


Figure S8. Solid-state  $^{13}\text{C}\{^1\text{H}\}$  CP NMR and  $^{31}\text{P}\{^1\text{H}\}$  CP NMR spectra of Ag-TPE-P4.

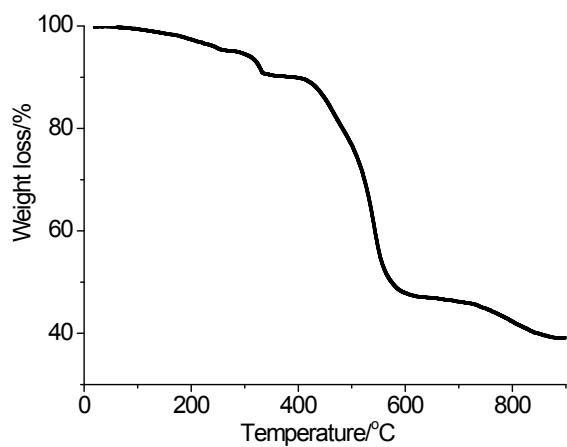


Figure S9. Thermogravimetric curve of Ag-TPE-P4.

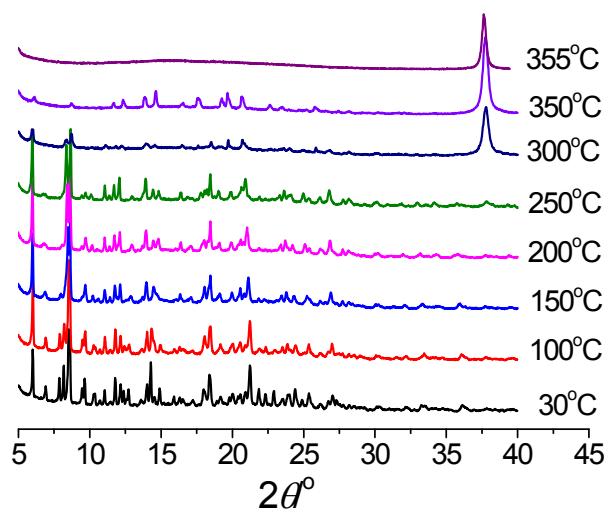


Figure S10. Temperature-dependent X-ray powder diffraction patterns of Ag-TPE-P4.

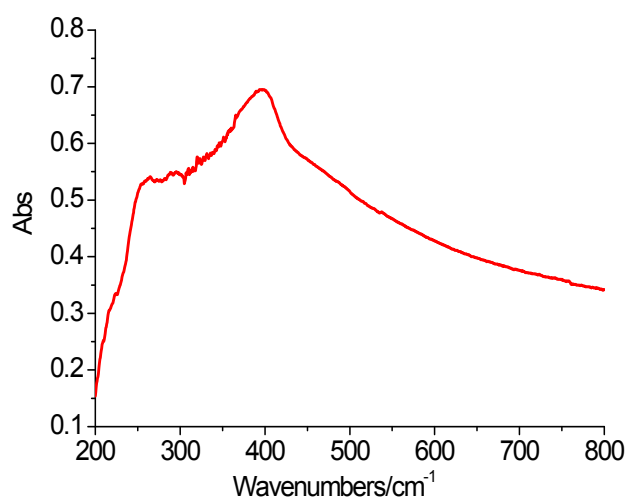


Figure S11. Solid-state UV-vis absorption spectrum of Ag-TPE-P4.

Table S1. Solid-state fluorescence lifetime data of TPE-P4, exposed to MeOH and after grinding.

	Sample	$\tau_1/\text{ns}^{[a]}$	$A_1^{[b]}$	$\tau_2/\text{ns}^{[a]}$	$A_2^{[b]}$	$\langle\tau\rangle/\text{ns}^{[c]}$
TPE-P4	Exposed to MeOH	1.44	0.59	3.24	0.41	2.18
	After grinding	2.12	0.48	3.91	0.52	3.06

[a] Fluorescence lifetime. [b] Fractional contribution. [c] Weighted mean lifetime

$$\langle\tau\rangle = \frac{A_1\tau_1 + A_2\tau_2}{A_1 + A_2}$$

Table S2. Selected bond lengths and bond angles for Ag-TPE-P4.

Bond length/Å			
Ag(1)-O(1)	2.407(7)	Ag(1)-P(1)	2.443(2)
Ag(1)-P(2)#1	2.457(2)	P(2)-Ag(1)#2	2.457(2)
C(38)-O(2)	1.221(15)	C(38)-O(1)#4	1.279(10)
C(38)-O(1)	1.279(10)	C(1)-C(1)#3	1.31(2)
Bond angle/°			
P(1)-Ag(1)-P(2)#1	135.31(7)	O(1)-Ag(1)-P(1)	107.3(2)
O(1)-Ag(1)-P(2)#1	115.0(2)	O(2)-C(38)-O(1)#4	122.6(6)
O(2)-C(38)-O(1)	122.6(6)	O(1)#4-C(38)-O(1)	114.9(12)
C(38)-O(1)-Ag(1)	109.2(6)		

Symmetry transformations used to generate equivalent atoms: #1  $x-1/3, x-y+1/3, z-1/6$   
 #2  $x+1/3, x-y+2/3, z+1/6$  #3  $y, x, -z+3/2$  #4  $-x, -x+y, -z+3/2$ .