

Supporting Information

Thermally populated “bright” states for wide-range and high temperature sensing in air

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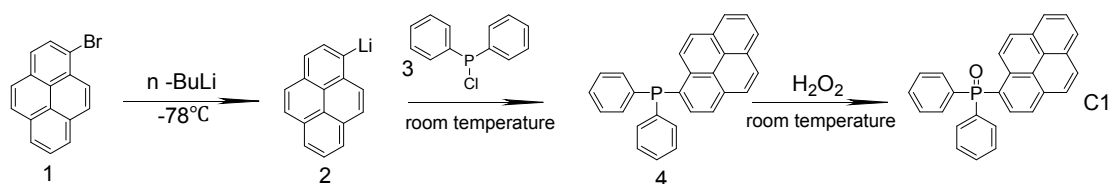
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Materials and Instruments: Chlorodiphenylphosphine, dichlorophenylphosphine and triethylphosphate were obtained from Alfa Aesar. Solvents in the experiment were distilled according to standard procedures before using. All chemical reactions were proceeded under the protection of the inert gases. ^1H NMR and ^{13}C NMR spectra were recorded on a Bruker Avance 400 spectrometer. MALDI-TOF-MS spectra were measured by a Bruker BIFLEX III spectrometer. Elemental analysis was performed by a Carlo Erba 1106. The absorption spectra were recorded on Hitachi UV-3010. The fluorescence spectra were collected on Hitachi F-4500. The concentrations of solution were 1.0×10^{-5} mol/L. The temperature of the sample was controlled with the help of a heating and cooling stage (HCS) from INSTEC. The fluorescence decay curves were performed on an Edinburgh FLS-920 instrument using single photon counting measurement (Samples were irradiated by Picoquant LDH-D-C-375 pulsed diode laser).

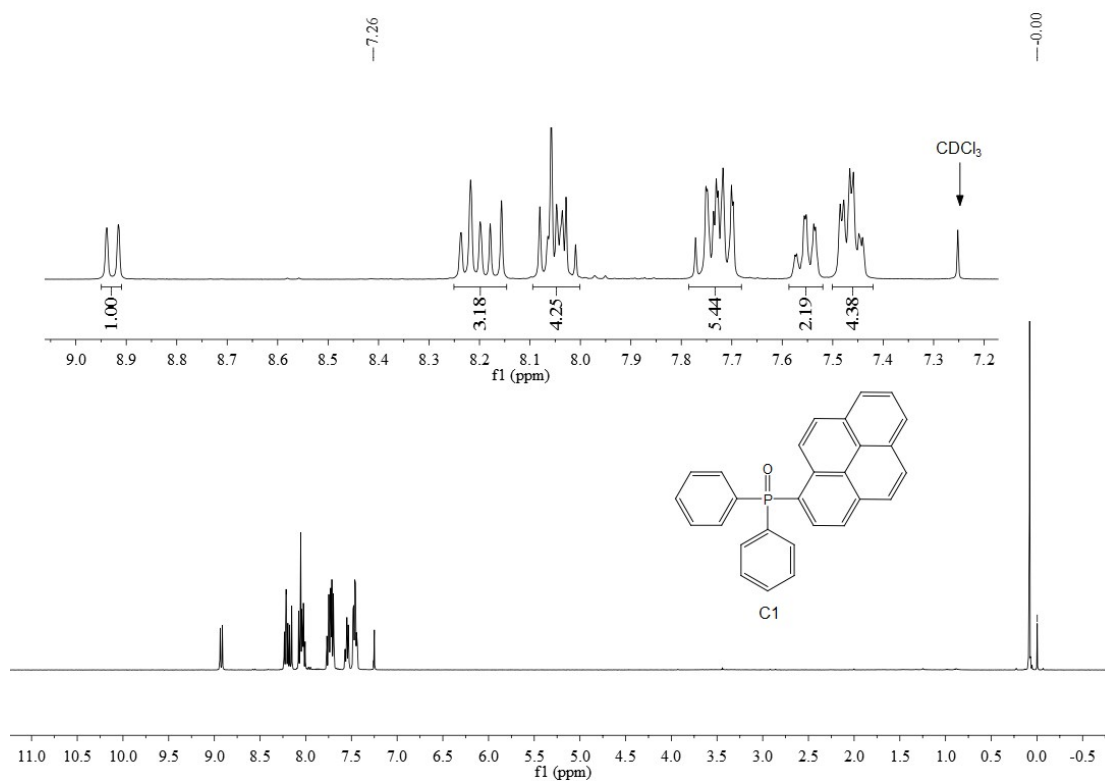
Computational methods: Geometry optimizations for the ground state and excited state of triaryphosphine oxide compounds molecule were carried using the ORCA software package with the DFT and TDDFT methods. B3LYP with the RIJCOSX approximation was employed here. All calculations above were employing basis set def2-svp and auxiliary basis set def2-svp/j.

Synthesis of diphenyl(pyren-1-yl)phosphine oxide (C1)

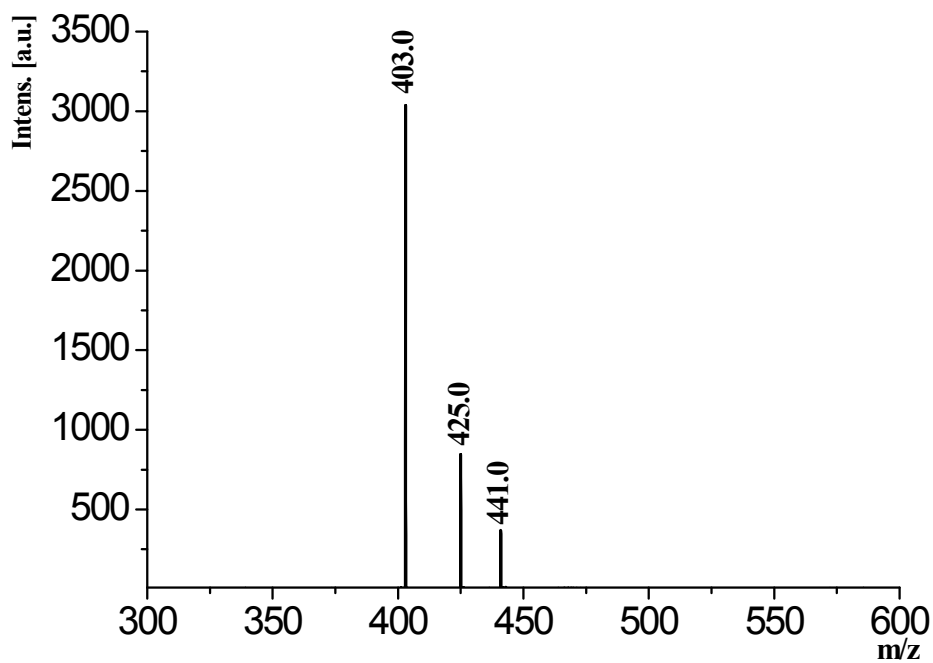
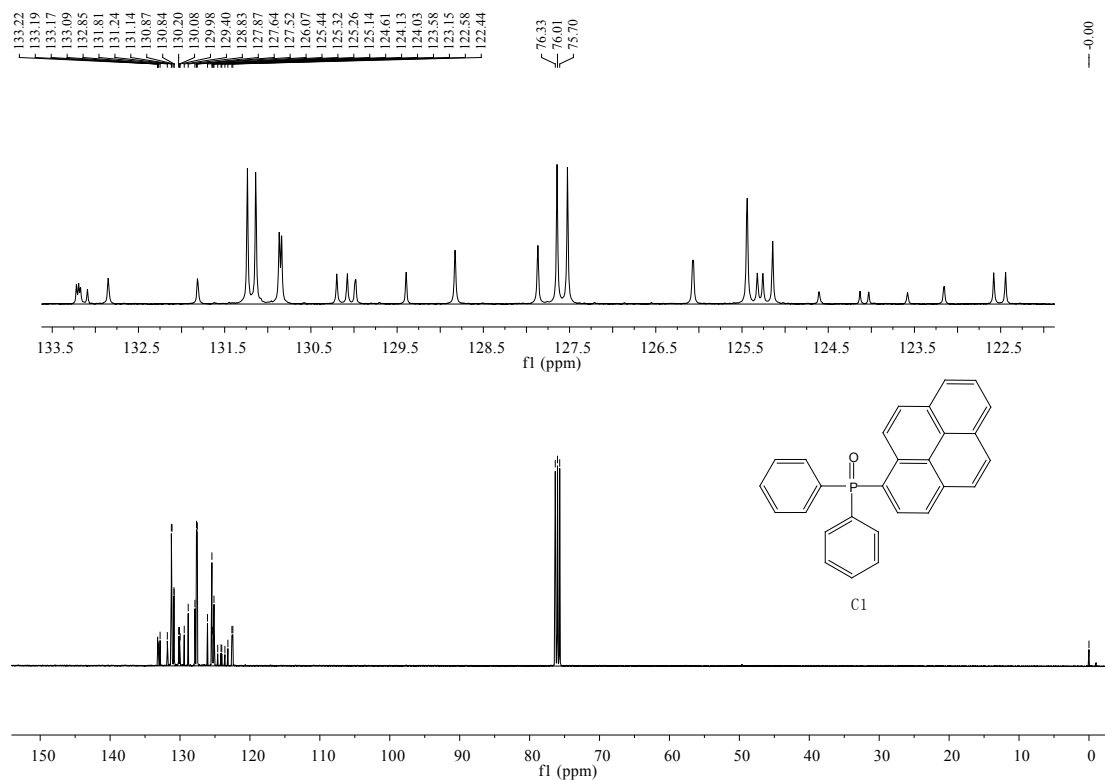


To a THF solution (80 ml) of 1-bromopyrene (2000 mg, 7.06 mmol) was added n-BuLi (5 ml, 7.76 mmol, 2.0 M in cyclohexane) at $-78\text{ }^\circ\text{C}$, which turned to a greenish suspension. After one hour, the temperature was allowed to naturally rise to room temperature. Stirring was then continued for a further hour. The mixture was then cooled again to $-78\text{ }^\circ\text{C}$ and chlorodiphenylphosphine (1710 mg, 7.76 mmol) was added by injection. The suspension was gradually warmed to ambient temperature and stirred for 2 h. After reaction finished, dry methanol (10 ml) was added. The organic compound was extracted with dichloromethane and the combined organic layer was dried over sodium sulfate, filtered and evaporated under reduced pressure to get a white solid. The residue obtained was dissolved in dichloromethane and H_2O_2 (10 ml, 30%) was added dropwise. After stirring for 4 h at room temperature, water (60 ml)

was added and the organic phase was extracted with dichloromethane (2× 40 ml), dried over anhydrous Na₂SO₄, filtered and the solvent was removed in vacuo. The crude reaction mixture was purified by column chromatography using hexane–ethyl acetate (1:3) as the eluent to afford C1, which was further purified by precipitating in chloroform and diethyl ether (1:2) mixture. Yield 60% (1.8 g); ¹H NMR (400 MHz, CDCl₃, ppm): δ 8.85 (d, J = 9.3 Hz, 1H), 8.21–8.07 (m, 3H), 8.07–7.92 (m, 4H), 7.74–7.61 (m, 5H), 7.61–7.28 (m, 6H). ¹³C NMR (400 MHz, CDCl₃, ppm): δ 133.21, 133.17, 133.09, 132.85, 131.81, 131.21, 131.14, 130.85, 130.20, 130.18, 129.98, 129.40, 127.87, 127.64, 127.52, 126.07, 125.39, 125.29, 125.21, 125.14, 124.64, 124.13, 124.03, 123.58, 123.15, 122.58, 122.36. MALDI-TOF m/z: 403.00 [M]⁺. Anal. calcd for C₂₈H₁₉PO (402.42): C, 83.57%; H, 4.76%; found: C, 83.31%; H, 4.53%.

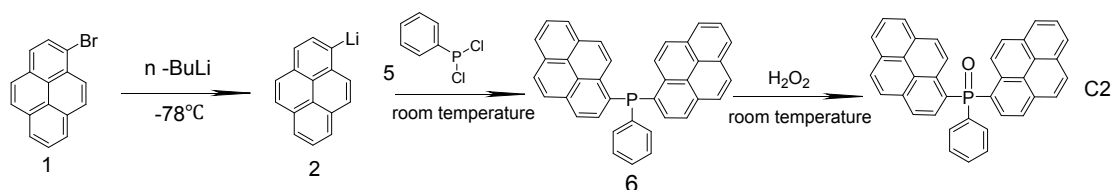


¹H-NMR spectrum of C1 in CDCl₃

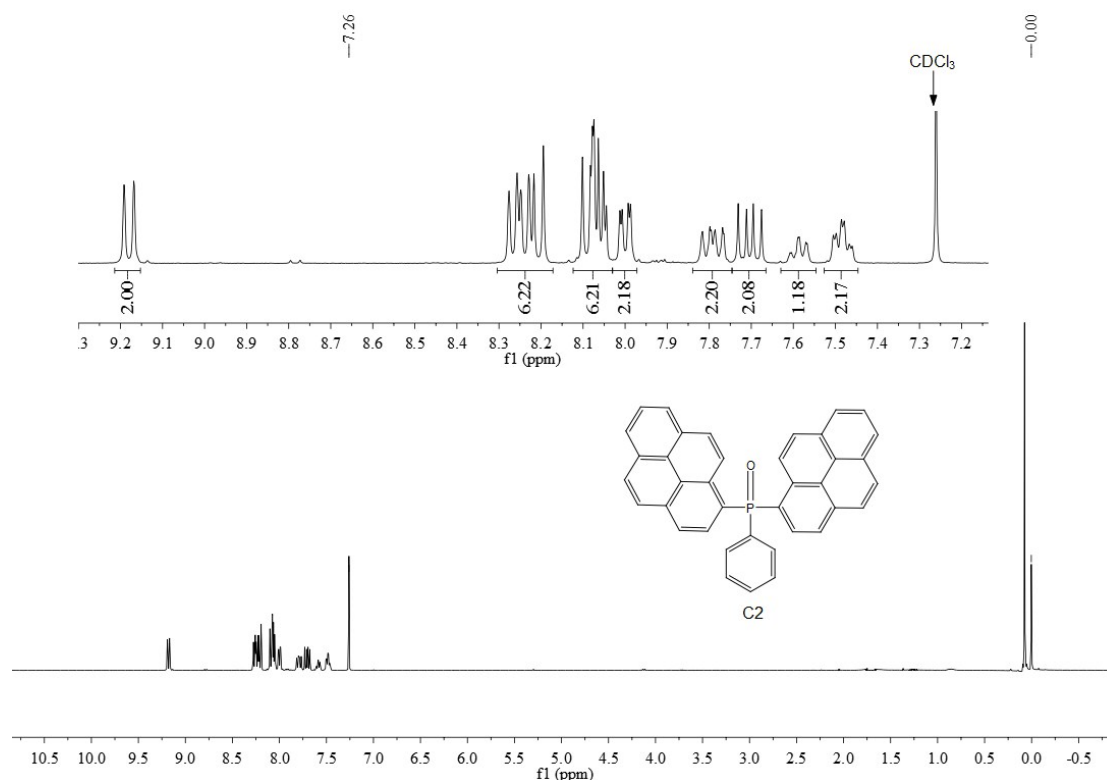


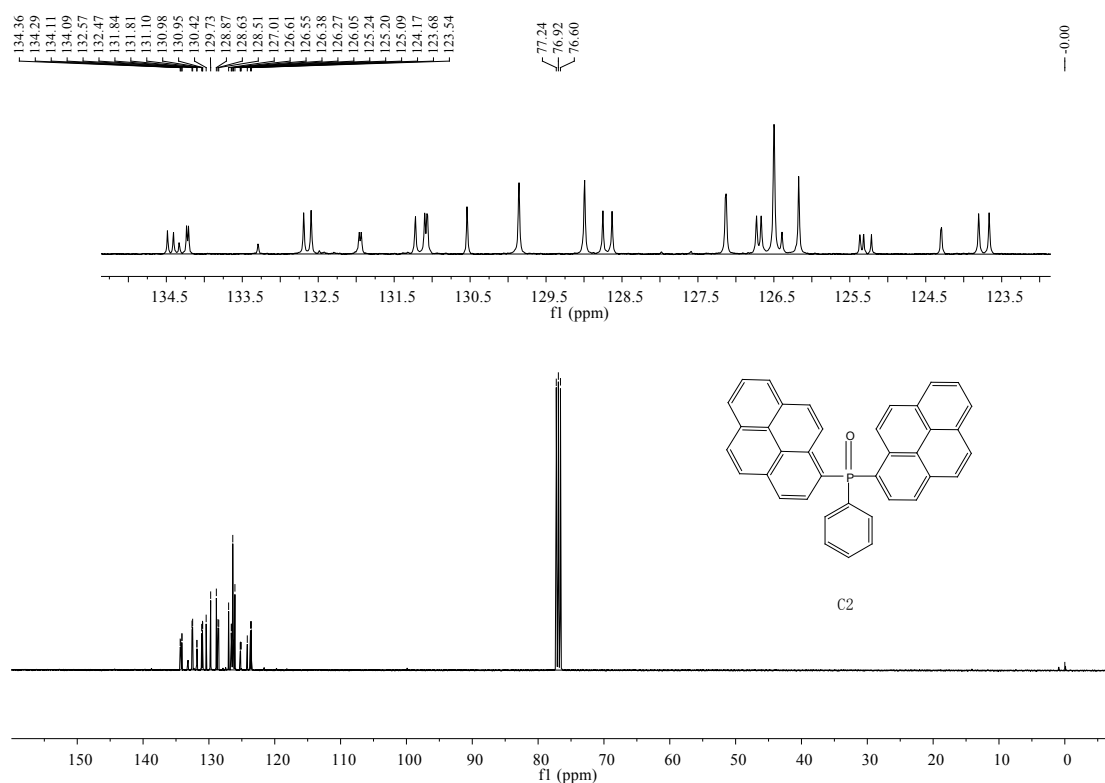
MALDI-TOF spectrum of C1

Synthesis of phenyldi(pyren-1-yl)phosphine oxide (C2)

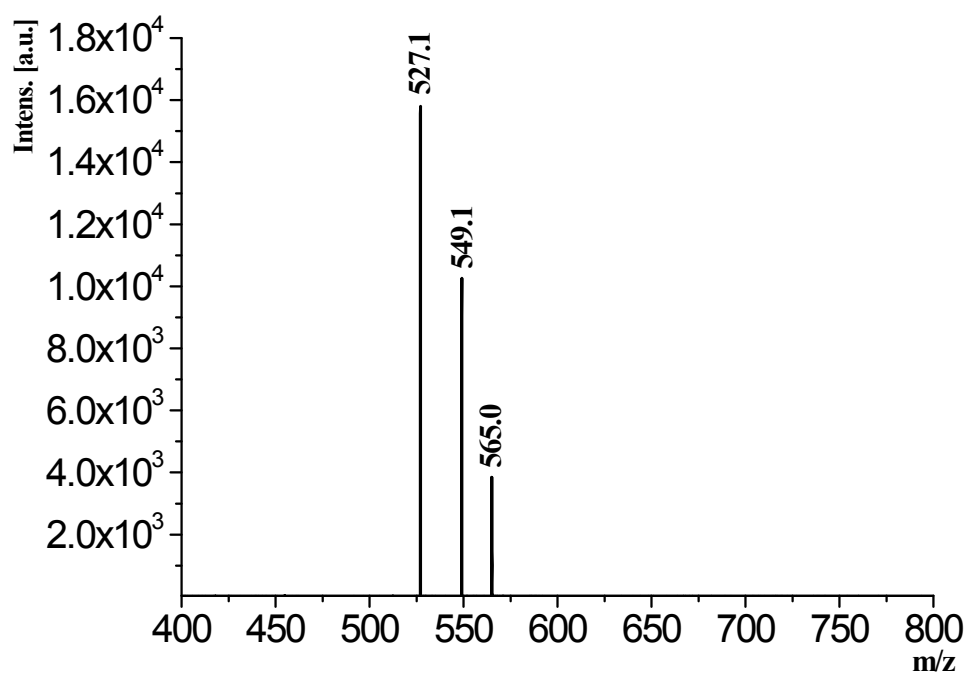


C2 was prepared according to a procedure similar to that of C1, using 1-bromopyrene (4000 mg, 14.12 mmol), n-BuLi (10 ml, 15.52 mmol, 2.0 M in cyclohexane) and dichlorophenylphosphine (1260 mg, 7.06 mmol) as the synthetic precursors. The obtained residue was purified by column chromatography (hexane–ethyl acetate 1:2) followed by precipitation in chloroform–diethyl ether (1:3). Yield 63% (2.3 g); ^1H NMR (400 MHz, CDCl_3 , ppm): δ 9.10 (d, $J = 9.3\text{Hz}$, 2H), 8.24–8.09 (m, 6H), 8.07–7.96 (m, 6H), 7.92 (d, $J = 10.1\text{Hz}$, 2H), 7.78–7.67 (m, 1H), 7.63 (d, $J = 7.9\text{Hz}$, 2H), 7.51 (t, $J = 6.8\text{Hz}$, 2H) 7.41 (t, $J = 7.6\text{Hz}$, 2H). ^{13}C NMR (400 MHz, CDCl_3 , ppm): δ 133.45, 133.37, 133.23, 133.20, 133.28, 132.26, 131.65, 131.55, 131.44, 131.34, 130.90, 130.80, 130.14, 130.04, 129.50, 128.80, 127.94, 127.71, 127.59, 126.93, 126.54, 126.08, 125.68, 125.62, 125.45, 125.35, 125.13, 124.31, 124.28, 124.18, 123.26, 122.76, 122.62, 120.69, 118.82, 117.27, 117.14. MALDI-TOF m/z : 527.10 $[\text{M}+\text{H}]^+$. Anal. calcd for $\text{C}_{38}\text{H}_{23}\text{PO}$ (526.15): C, 86.68; H, 4.40%; found: C, 88.51; H, 4.23%.



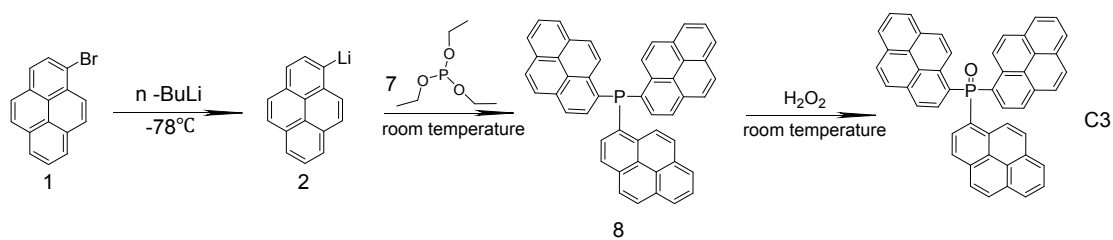


¹³C-NMR spectrum of C2 in CDCl₃.

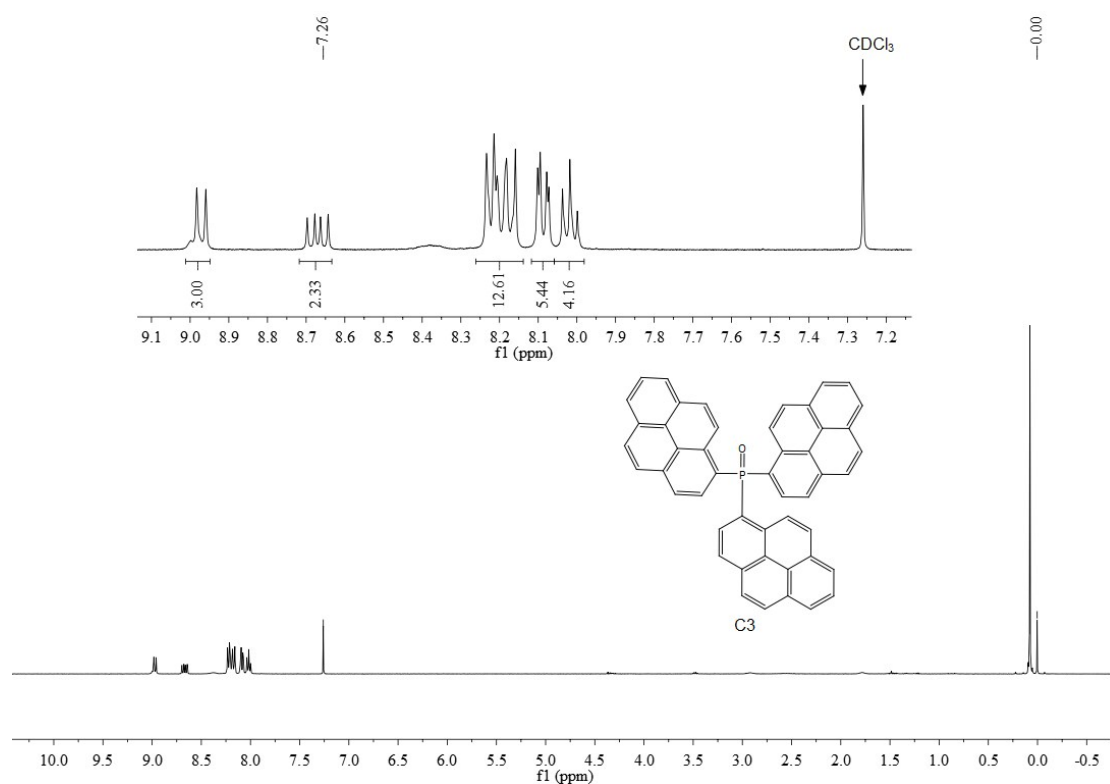


MALDI-TOF spectrum of C2

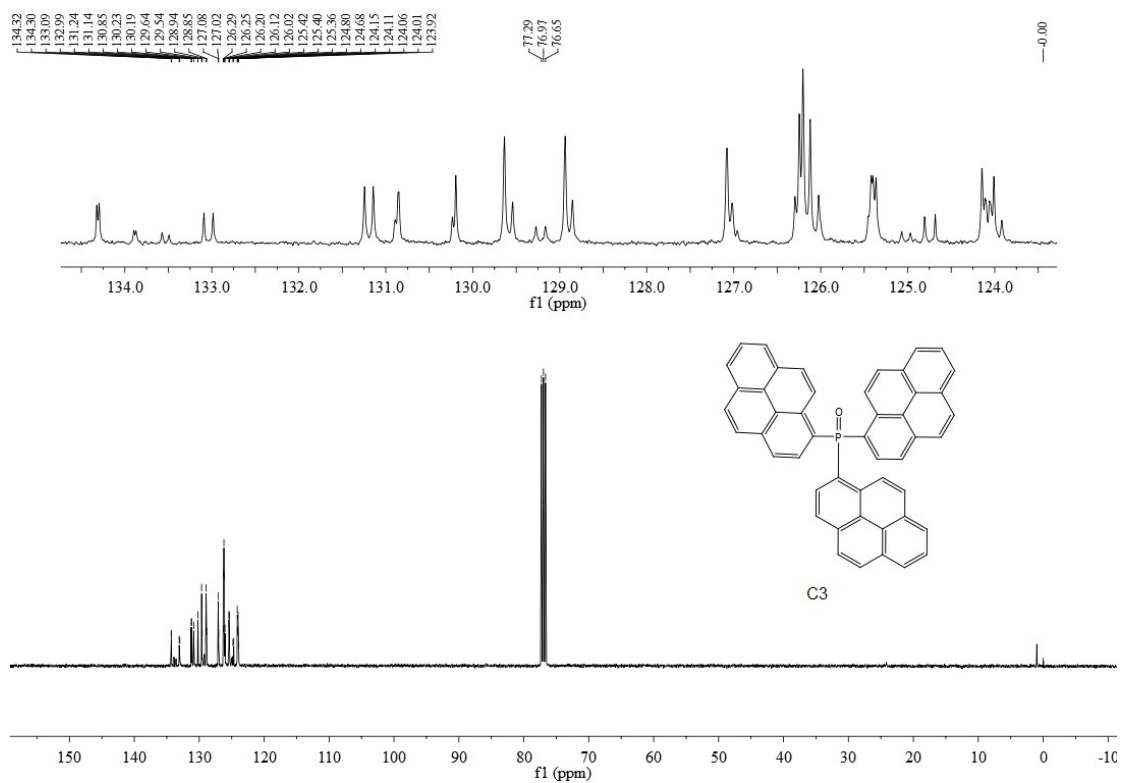
Synthesis of tri(pyren-1-yl)phosphine oxide (C3)



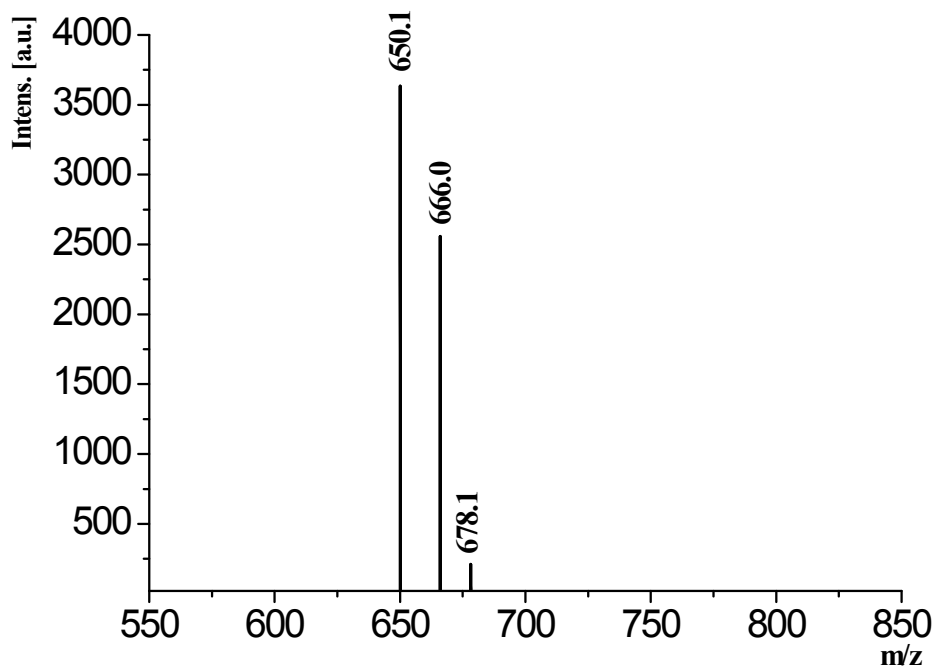
C3 was prepared according to a procedure similar to that of C1, using 1-bromopyrene (6000 mg, 21.18 mmol), n-BuLi (15 ml, 3.28 mmol, 2.0 M in cyclohexane) and triethylphosphate (1260 mg, 7.06 mmol) as the synthetic precursors. The obtained residue was purified by column chromatography (hexane–ethyl acetate 1:2) followed by precipitation in chloroform–diethyl ether (1:3). Yield 58% (2.7 g); ^1H NMR (400 MHz, CDCl_3 , ppm): δ 8.74–8.63 (t, $J = 8.6\text{Hz}$, 3H), 8.32 (dd, $J = 15.7$, 7.8Hz, 2H), 8.23–8.10 (m, 10H), 8.10–7.93 (m, 8H), 7.68–7.57 (t, $J = 7.8\text{Hz}$, 2H), 7.54–7.44 (t, $J = 7.8\text{Hz}$, 2H). ^{13}C NMR (400 MHz, CDCl_3 , ppm): δ 151.95, 139.64, 134.33, 134.23, 133.67, 133.53, 132.62, 132.53, 131.00, 130.30, 130.25, 130.20, 130.15, 130.08, 139.91, 129.80, 129.55, 128.49, 127.62, 127.37, 127.15, 127.10, 126.93, 126.48, 126.38, 126.22, 126.11, 125.64, 125.37, 125.23, 125.09, 124.71, 124.66, 124.36, 124.25, 124.16, 123.90, 123.77. MALDI-TOF m/z : 650.10 $[\text{M}]^+$. Anal. calcd for $\text{C}_{48}\text{H}_{27}\text{PO}$ (650.18): C, 88.60; H, 4.18%; found: C, 88.76; H, 4.13%.



^1H -NMR spectrum of C3 in CDCl_3



¹³C-NMR spectrum of C3 in CDCl₃



MALDI-TOF spectrum of C3

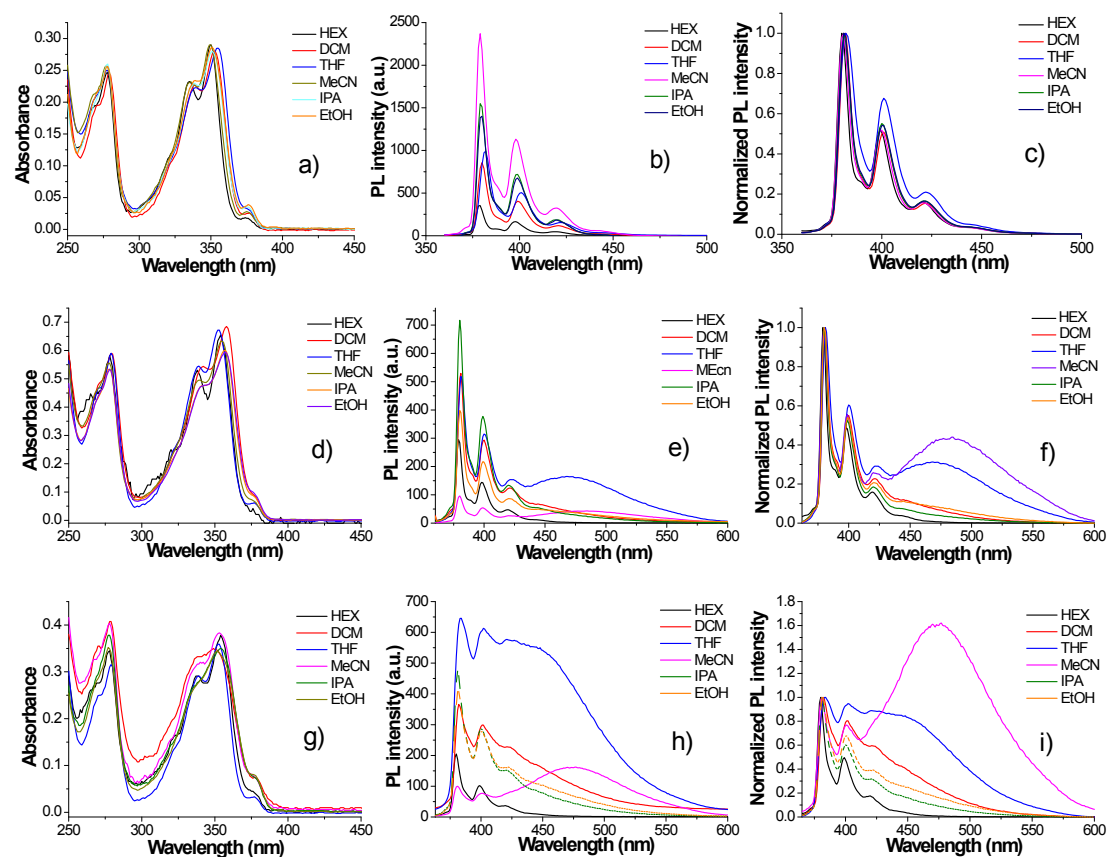


Figure S1. The absorption, fluorescence spectra and normalized fluorescence spectra of C1 (a, b and c), C2 (d, e and f), and C3 (g, h and i) in various solvents (1.0×10^{-5} mol/L) at room temperature.

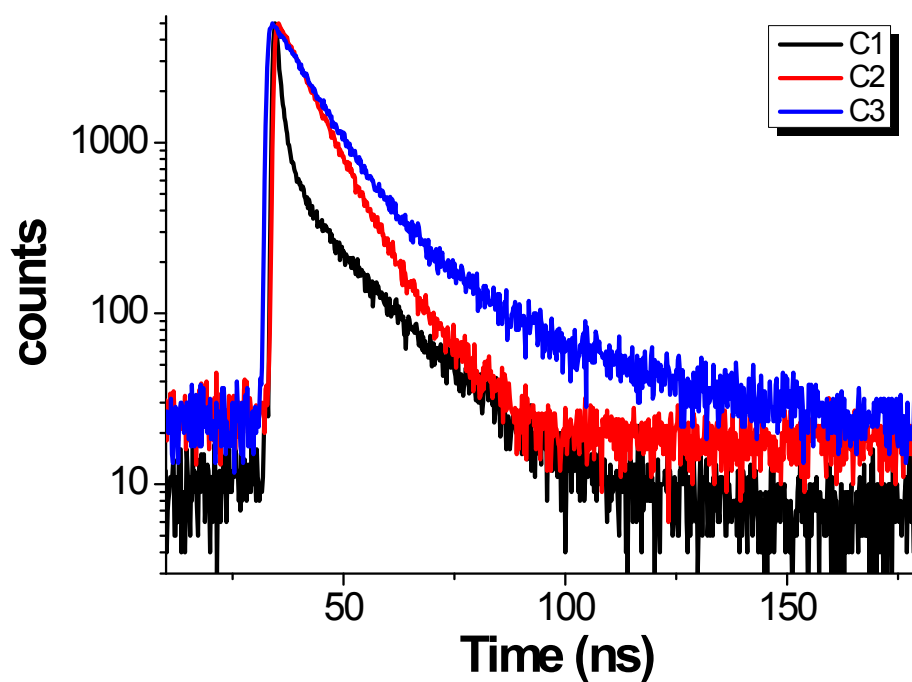


Figure S2. PL decay spectrum of C1, C2 and C3 detected at 450 nm in MOE (1.0×10^{-5} mol/L) at room temperature.

Table S1. Fitting data of the fluorescence decay of C1, C2 and C3 in MOE (1.0×10^{-5} mol/L) at room temperature, detected at 450 nm.

	τ_1 /ns	τ_2 /ns	$\langle\tau\rangle^a$ /ns	χ^2
C1	12 (100%)	-	12	1.016
C2	7.8 (92.12%)	17.5 (7.88%)	8.56	1.085
C3	9.5 (80.56%)	32.3 (19.44%)	13.93	1.051

^a the average lifetime

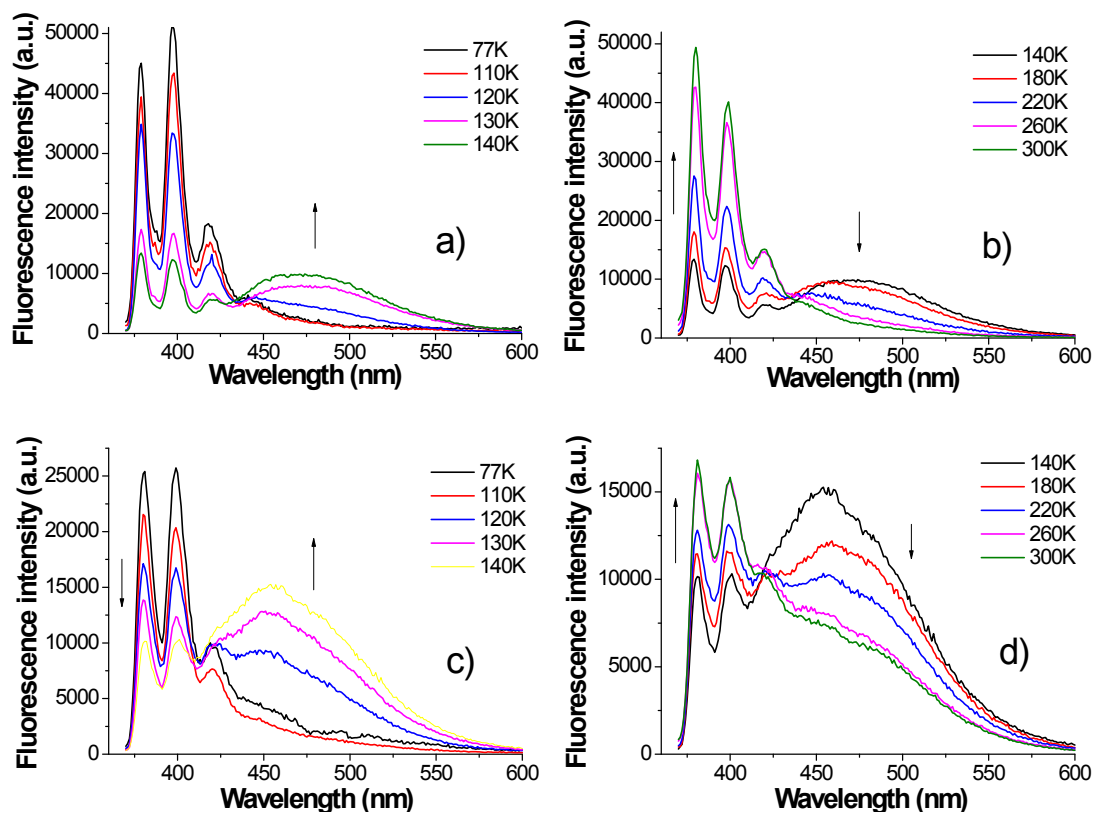
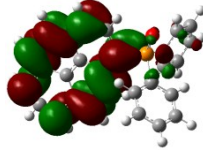
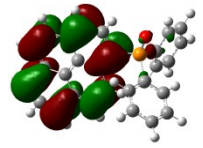
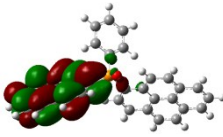
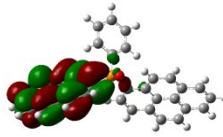
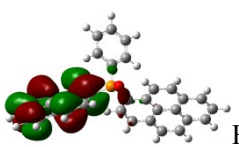
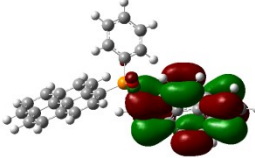
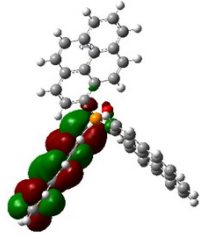
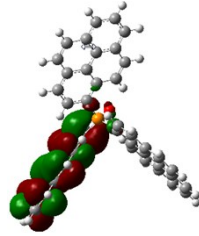
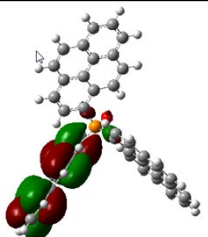
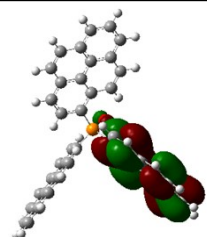


Figure S3. Emission spectra of the C2 (a, b) and C3 (c, d) in 2-Methyltetrahydrofuran solvent (1.0×10^{-5} mol/L) by changing the temperature from 77 to 300K.

Table S2. TDDFT calculated results of C1、C2 and C3

	LE state	CT state
Wavelength	380.05 nm	—
f^a	0.4093	—
transition	HOMO→LUMO (95%)	—
C1	 LUMO	—
	 HOMO	—
Wavelength	380.71 nm	508.94 nm
f^a	0.7233	$f=0.0190$
transition	HOMO-1→LUMO (78%)	HOMO→LUMO (99%)
C2	 LUMO	 LUMO
	 HOMO-1	 HOMO
Wavelength	381.44 nm	506.71 nm
f^a	0.4674	0.0006
Transition	HOMO-2 → LUMO (78%)	HOMO → LUMO (100%)
C3	 LUMO	 LUMO
	 HOMO-2	 HOMO

a) Oscillator strength

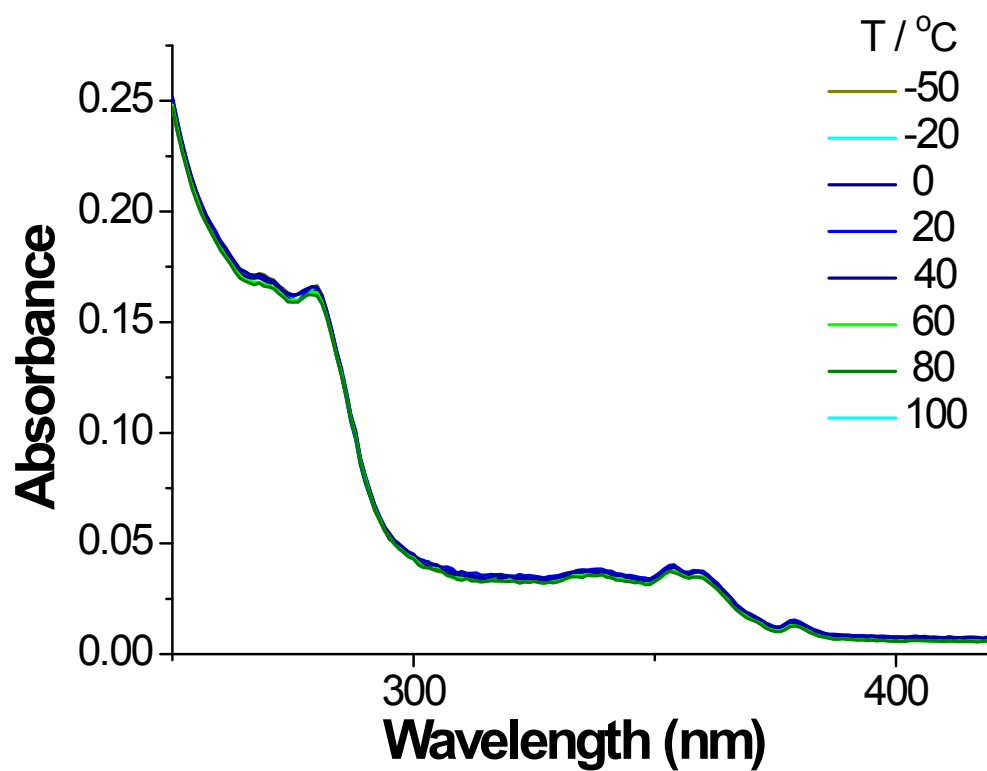


Figure S4. Absorption spectra of the C3 in MOE (5.0×10^{-6} mol/L) at gradually increasing temperatures.

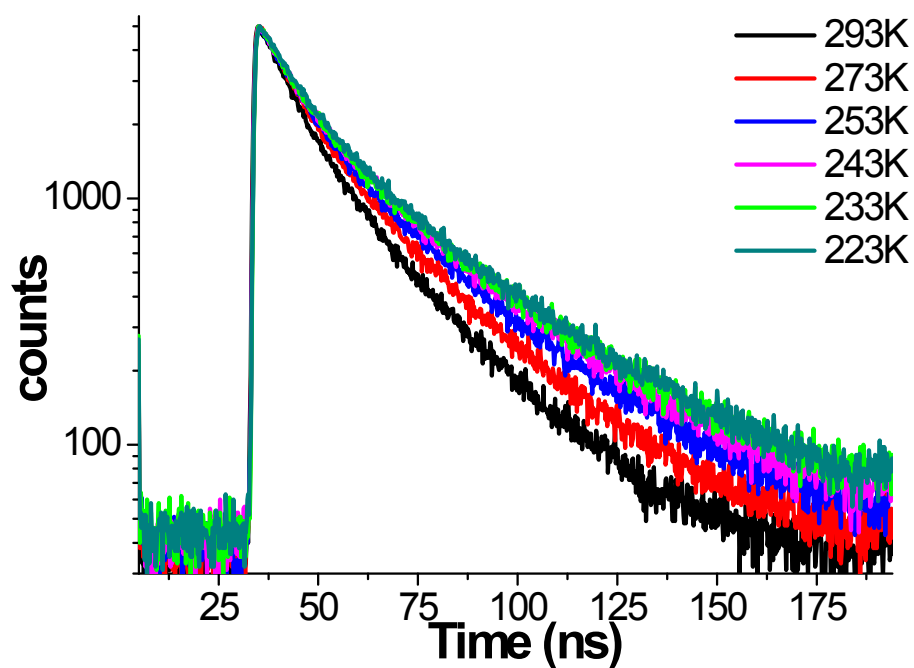


Figure S5. PL decay spectrum of C3 detected at 500 nm in MOE (1.0×10^{-5} mol/L) at gradually reduce temperatures form 223 to 293K.

Table S3. Fitting data of the fluorescence decay of C3 in MOE (1.0×10^{-5} mol/L) at gradually reduce temperatures form 293K to 223K.

T/K	τ^1 /ns	τ^2 /ns	$\langle\tau\rangle^a$ /ns	χ^2
293	9.34 (58.3%)	30.49 (41.7%)	18.16	1.093
273	9.68 (44.0%)	28.63 (56.0%)	20.29	0.939
253	9.18 (31.5%)	32.11 (68.5%)	24.88	1.014
243	10.00 (28.6%)	32.54 (71.4%)	26.09	1.141
233	9.41 (25.8%)	34.73 (74.2%)	28.19	1.111
223	9.34(25.1%)	34.73 (74.9%)	28.35	1.094

^a the average lifetime

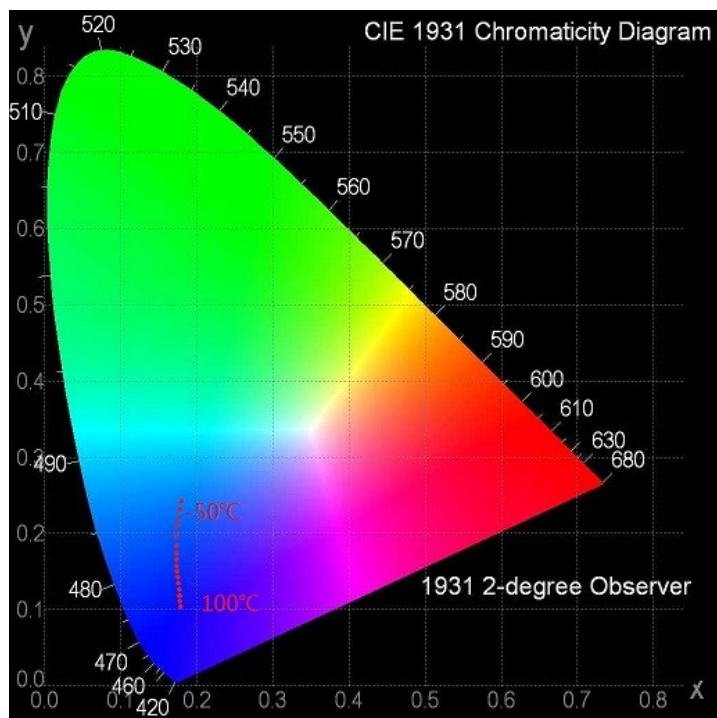


Figure S6. CIE chromaticity diagram showing the temperature dependence of the (x, y) color coordinates of C3-MOE system.

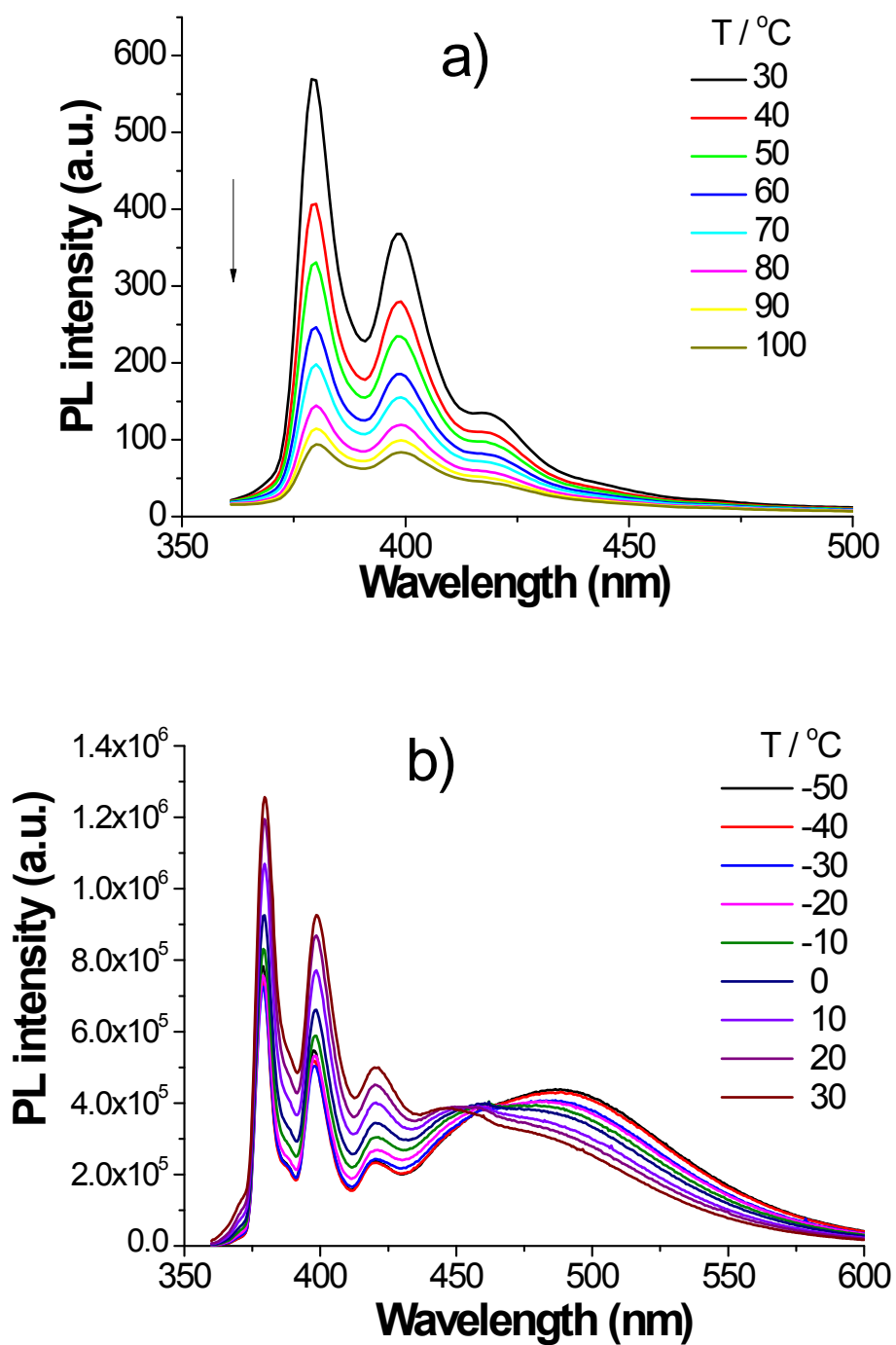


Figure S7. Temperature-dependent emission spectra of C1 (a) and C2 (b) in MOE (1.0×10^{-5} mol/L) with excitation wavelength of 360 nm.