

Supporting Information

One-Step Synthesis of Imidazoline-Containing Macrocycles and Their Complexation with Fullerenes C₆₀ and C₇₀

Fan Yang, Zhigang Wang, Feijie Song, Xingyan Liu, Jingbo Lan, and Jingsong You**

*Key Laboratory of Green Chemistry and Technology of Ministry of Education, College of Chemistry,
and State Key Laboratory of Biotherapy, West China Medical School,
Sichuan University, 29 Wangjiang Road, Chengdu 610064, PR China
Fax: 86-28-85412203; E-mail: fsong@scu.edu.cn, jsyou@scu.edu.cn*

Table of contents

I. General remarks.....	S3
II. Synthesis of the imidazoline-containing macrocycles 3	S3
III. Copies of the ESI-MS spectra of 3a and 3b	S6
IV. The single crystal structure of macrocycle 3b	S7
V. Photophysical properties of 3	S8
VI. Binding studies of 3 with fullerenes.....	S8
VII. References.....	S15
VIII. Copies of ¹ H and ¹³ C NMR spectra.....	S16

I. General remarks

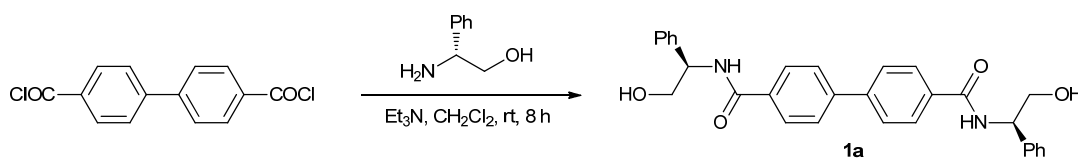
NMR spectra were obtained on a Bruker AV II-400 or a Varian Inova 400 spectrometer. The ^1H NMR (400 MHz) chemical shifts were measured relative to CDCl_3 , TMS or $\text{DMSO-}d_6$ (CDCl_3 : $\delta = 7.26$ ppm; TMS: $\delta = 0.00$ ppm; $\text{DMSO-}d_6$: $\delta = 2.50$ ppm). The ^{13}C NMR (100 MHz) chemical shifts were given using CDCl_3 or $\text{DMSO-}d_6$ as the internal standard (CDCl_3 : $\delta = 77.16$ ppm; $\text{DMSO-}d_6$: $\delta = 39.52$ ppm). High-resolution mass spectra (HRMS) were obtained with a Waters-Q-TOF Premier (ESI). X-Ray single-crystal diffraction data were collected on a Bruker SMART 1000 CCD area detector diffractometer. Melting points were determined with XRC-1 instrument and are uncorrected. The optical rotations were determined on a Perkin-Elmer Polarimeter-341 and reported as follows: $[\alpha]_D^{25}$: ($c = \text{g}/100 \text{ mL}$, in solvent). Absorption spectra were obtained on a HITACHI U-2910 spectrophotometer. Fluorescence spectra were collected on a Horiba Jobin Yvon-Edison Fluoromax-4 fluorescence spectrometer.

Unless otherwise noted, all reagents were obtained from commercial suppliers and were used without further purification. CHCl_3 was purified by washing with water, dried over CaCl_2 , and distilled from P_2O_5 and stored in the dark under an N_2 atmosphere. Et_3N and THF were distilled from CaH_2 and sodium/benzophenone, respectively, and stored under nitrogen. Unless otherwise indicated, all manipulations were carried out under an N_2 atmosphere. Amino alcohols¹ and biphenyl-4,4'-dicarbonyl dichloride² were prepared according to the literature procedures.

II. Synthesis of the imidazoline-containing macrocycles **3a** and **3b**³

i. Synthesis of macrocycle (*R,R,R,R*)-**3a**

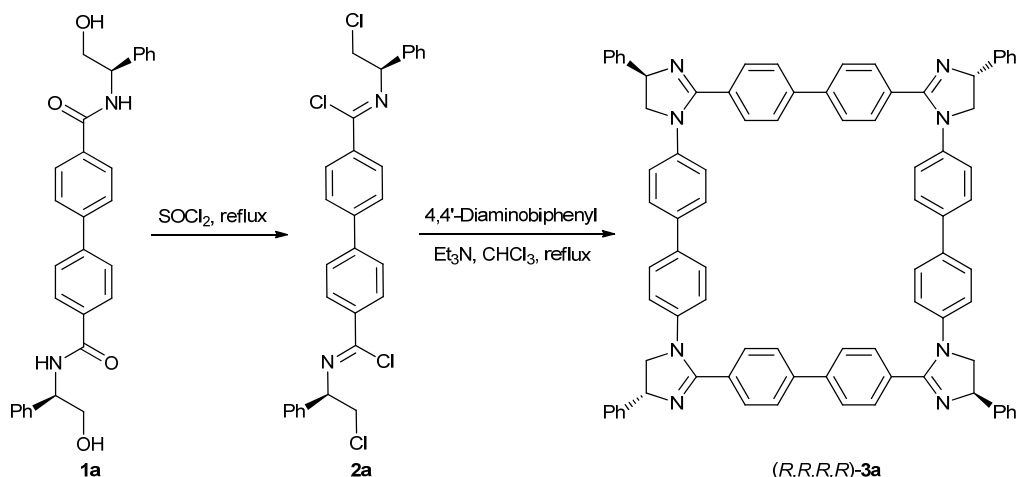
N,N'-Bis((*R*)-2-hydroxy-1-phenylethyl)-[1,1'-biphenyl]-4,4'-dicarboxamide (**1a**)



A solution of (*R*)-phenylglycinol (5.2 g, 38 mmol) and triethylamine (6.2 mL, 45 mmol) in CH_2Cl_2 (80 mL) was added dropwise to a stirred solution of biphenyl-4,4'-dicarbonyl dichloride (5.02 g, 18 mmol) in CH_2Cl_2 (80 mL) at 0°C . The resulting solution was warmed to room temperature and stirred at room temperature for 12 h, during which time a lot of white solids precipitated. Water (100 mL) was added to the resulting mixture to dissolve the salts and the remaining solids were filtered off, and washed with water to give the desired bis(amido) alcohol **1a** as a white solid (8.46 g, 98%

yield). M.p.: > 250 °C. $[\alpha]_D^{23} = 78.8$ (c = 0.56, DMSO). $^1\text{H NMR}$ (400 MHz, DMSO- d_6): δ 3.65-3.69 (m, 2H), 3.72-3.77 (m, 2H), 5.07-5.12 (m, 4H), 7.24 (t, $J = 7.6$ Hz, 2H), 7.33 (t, $J = 8.0$ Hz, 4H), 7.41 (d, $J = 7.6$ Hz, 4H), 7.85 (d, $J = 8.0$ Hz, 4H), 8.04 (d, $J = 8.0$ Hz, 4H), 8.85 (d, $J = 8.4$ Hz, 2H) ppm. $^{13}\text{C NMR}$ (100 MHz, DMSO- d_6): δ 56.4, 64.7, 126.9, 127.1, 127.2, 128.4, 134.1, 141.5, 142.0, 166.2 ppm. HRMS (ESI $^+$): calcd for $\text{C}_{30}\text{H}_{28}\text{N}_2\text{NaO}_4$ $[\text{M}+\text{Na}]^+$ 503.1947, found 503.1947.

Macrocycle (*R,R,R,R*)-**3a**



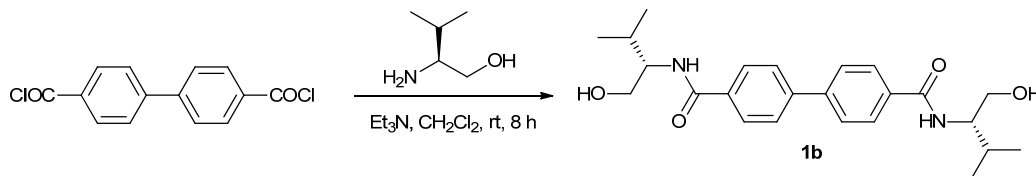
Bis(amido) alcohol **1a** (0.96 g, 2 mmol) was dissolved in SOCl_2 (5 mL) and heated under reflux for 8 h. The volatile was then removed under reduced pressure to afford the crude tetrachloride **2a**, which was used immediately for the next step without purification.

A mixture of CHCl_3 (20 mL) and Et_3N (2.6 mL, 18.6 mmol) was heated to reflux. The solution of **2a** in CHCl_3 (30 mL) and the solution of 4,4'-diaminobiphenyl (0.41 g, 2.2 mmol) in CHCl_3 (30 mL) were simultaneously added dropwise to this mixture at the same speed (1-2 drops/sec) under reflux. The resulting solution was stirred under reflux for 18 h. Then 10% NaOH aqueous solution (10 mL) was added and the mixture was extracted with CH_2Cl_2 (3×10 mL). The combined organic phases were dried over MgSO_4 , and evaporated, and the residue was purified by column chromatography on silica gel (CH_2Cl_2 /petroleum ether/acetone = 1/1/1, v/v/v) to afford (*R,R,R,R*)-**3a** as a light yellow solid (120.7 mg) in 10% overall yield based on starting material **1a**. M.p.: 198-200 °C. $[\alpha]_D^{23} = 77.1$ (c = 0.38, CHCl_3). $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 4.02 (t, $J = 8.8$ Hz, 4H), 4.53 (t, $J = 10.0$ Hz, 4H), 5.39 (t, $J = 9.2$ Hz, 4H), 6.85 (d, $J = 8.0$ Hz, 8H), 7.28-7.32 (m, 12H), 7.37 (t, $J = 7.2$ Hz, 8H), 7.41 (d, $J = 7.6$ Hz, 8H), 7.53 (d, $J = 8.4$ Hz, 8H), 7.69 (d, $J = 8.0$ Hz, 8H) ppm. $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 61.5, 67.5, 122.4, 126.9, 127.0, 127.2, 127.4, 128.8, 129.7, 130.0, 135.5, 141.5, 142.3, 143.7, 161.3 ppm. HRMS (ESI $^+$): calcd for $\text{C}_{84}\text{H}_{65}\text{N}_8$ $[\text{M}+\text{H}]^+$ 1185.5332, found 1185.5330.

When the reaction was run on 40 mmol scale, 2.2 g of (*R,R,R,R*)-**3a** was obtained in 9% overall yield.

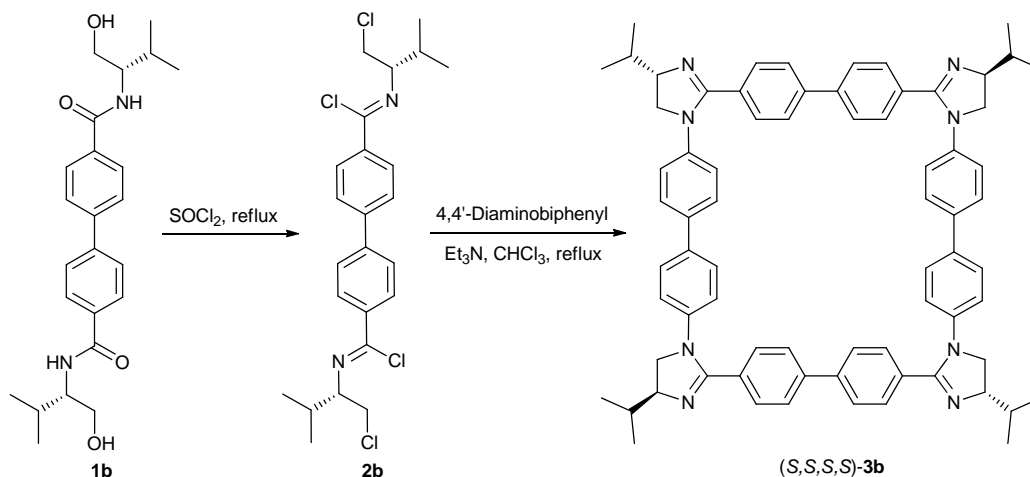
ii. Synthesis of macrocycle (*S,S,S,S*)-**3b**

*N*⁴,*N*^{4'}-Bis((*S*)-1-hydroxy-3-methylbutan-2-yl)-[1,1'-biphenyl]-4,4'-dicarboxamide (**1b**)



Following the same procedure as **1a**. (*S*)-valinol (3.9 g, 38 mmol) instead of (*R*)-phenylglycinol was used. Compound (*S*)-**1b** was obtained as a white solid (6.97 g, 94% yield). M.p.: > 250 °C. $[\alpha]_D^{23} = -7.5$ ($c = 0.32$, DMSO). ¹H NMR (400 MHz, DMSO-*d*₆): δ 0.89 (d, $J = 6.8$ Hz, 6H), 0.92 (d, $J = 6.8$ Hz, 6H), 1.90-1.99 (m, 2H), 3.54 (d, $J = 5.2$ Hz, 4H), 3.81-3.87 (m, 2H), 4.67 (br. s, 2H), 7.82 (d, $J = 8.0$ Hz, 4H), 7.99 (d, $J = 8.4$ Hz, 4H), 8.09 (d, $J = 8.8$ Hz, 2H) ppm. ¹³C NMR (100 MHz, DMSO-*d*₆): δ 18.8, 19.8, 28.7, 56.8, 61.4, 126.6, 128.2, 134.4, 141.6, 166.2 ppm. HRMS (ESI⁺): calcd for C₂₄H₃₂N₂NaO₄ [M+Na]⁺ 435.2260, found 435.2258.

Macrocycle (*S,S,S,S*)-**3b**



Following the same procedure as (*R,R,R,R*)-**3a**. Bis(amido) alcohol **1b** (0.82 g, 2 mmol) instead of **1a** was used. Purification by column chromatography on silica gel (CH₂Cl₂/petroleum ether/acetone = 1/1/1, v/v/v) afforded (*S,S,S,S*)-**3b** as a light yellow solid in 14% overall yield based on starting material **1b** (147.8 mg). M.p.: > 250 °C. $[\alpha]_D^{23} = -7.3$ ($c = 0.3$, CHCl₃). ¹H NMR (400 MHz, CDCl₃): δ 0.97 (d, $J = 6.4$ Hz, 12H), 1.06 (d, $J = 6.4$ Hz, 12H), 1.93-1.97 (m, 4H), 3.77 (t, $J = 6.4$ Hz, 4H), 4.06-4.16 (m, 8H), 6.78 (d, $J = 8.0$ Hz, 8H), 7.27 (d, $J = 7.6$ Hz, 8H), 7.48 (d, $J = 8.0$ Hz, 8H), 7.58 (d, $J = 7.6$ Hz, 8H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ 18.0, 19.0, 33.2, 56.0, 70.0, 122.0, 126.9,

127.0, 129.4, 130.4, 135.0, 141.8, 142.0, 160.2 ppm. HRMS (ESI⁺): calcd for C₇₂H₇₃N₈ [M+H]⁺ 1049.5958, found 1049.5957.

When the reaction was run on 40 mmol scale, 2.7 g of (*S,S,S,S*)-**3b** was obtained in 13% overall yield.

III. Copies of the ESI-MS spectra of **3a** and **3b**

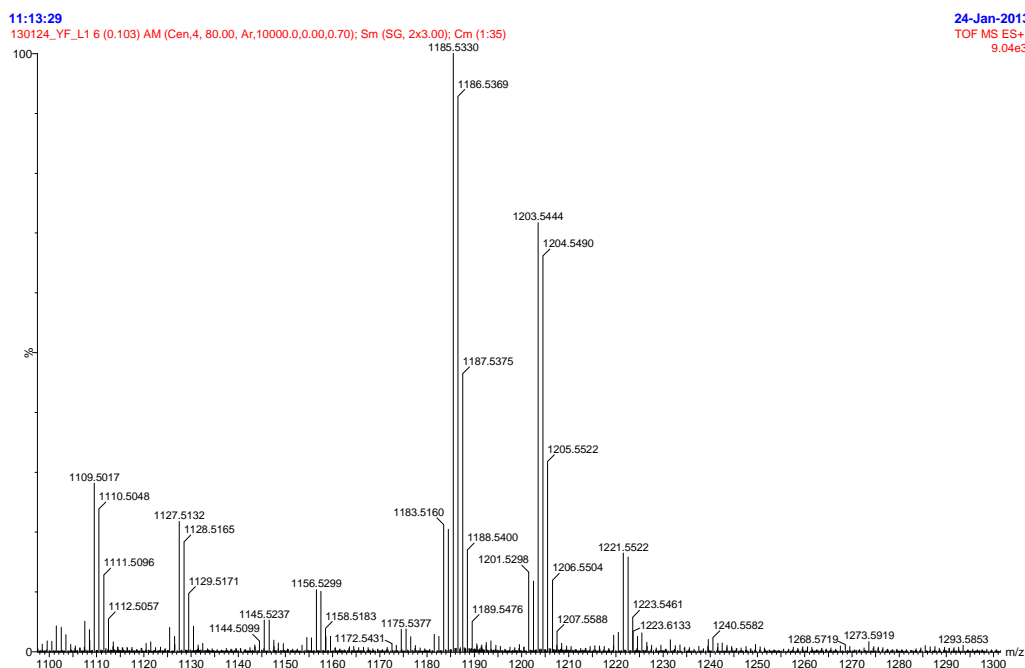


Fig. S1 HR-ESI mass spectrum of **3a**

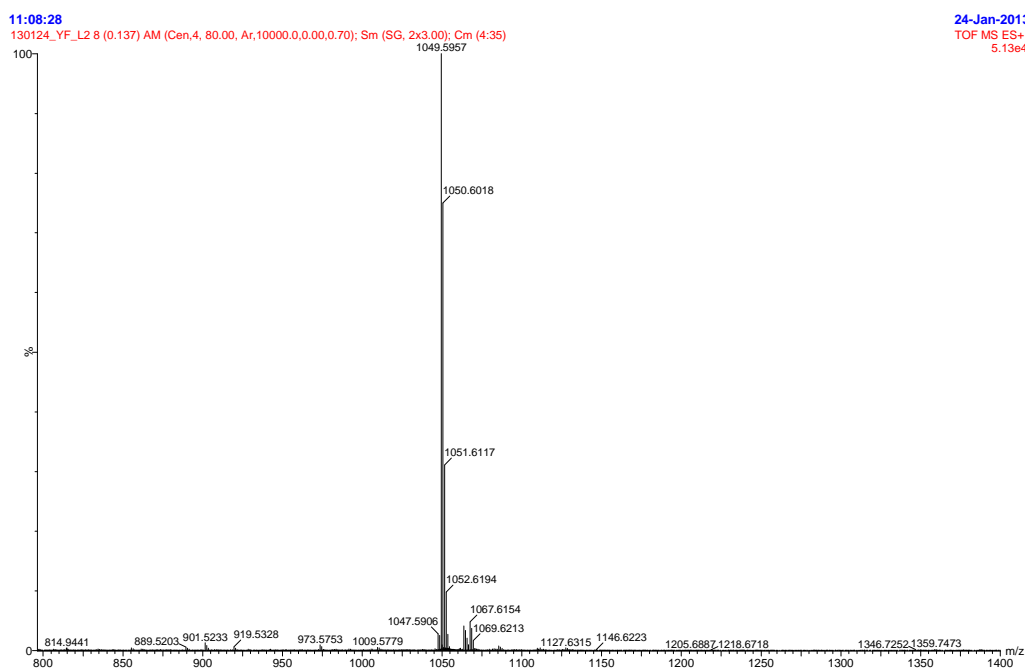


Fig. S2 HR-ESI mass spectrum of **3b**

IV. The single crystal structure of macrocycle **3b**

Table S1 Crystallographic data of **3b**

Empirical formula	C ₇₂ H ₇₂ N ₈	F(000)	1120.0
Formula weight	1049.38	Crystal size/mm ³	0.48 × 0.40 × 0.16
Temperature/K	110.0	2 θ range for data collection	2.76 to 26.37°
Crystal system	monoclinic	Index ranges	-15 ≤ h ≤ 5, -26 ≤ k ≤ 16, -21 ≤ l ≤ 21
Space group	P2 ₁	Reflections collected	18820
a/Å	12.1030(11)	Independent reflections	13037[R(int) = 0.0757]
b/Å	21.0076(13)	Data/restraints/parameters	13037/1/731
c/Å	16.8156(9)	Goodness-of-fit on F ²	0.697
α /°	90.00	Final R indexes [I ≥ 2 σ (I)]	R ₁ = 0.0671, wR ₂ = 0.1354
β /°	97.335(6)	Final R indexes [all data]	R ₁ = 0.1635, wR ₂ = 0.1544
γ /°	90.00	Largest diff. peak/hole / e Å ⁻³	0.178/-0.143
Volume/Å ³	4240.5(5)		
Z	2		
ρ_{calc} mg/mm ³	0.822		
m/mm ⁻¹	0.049		

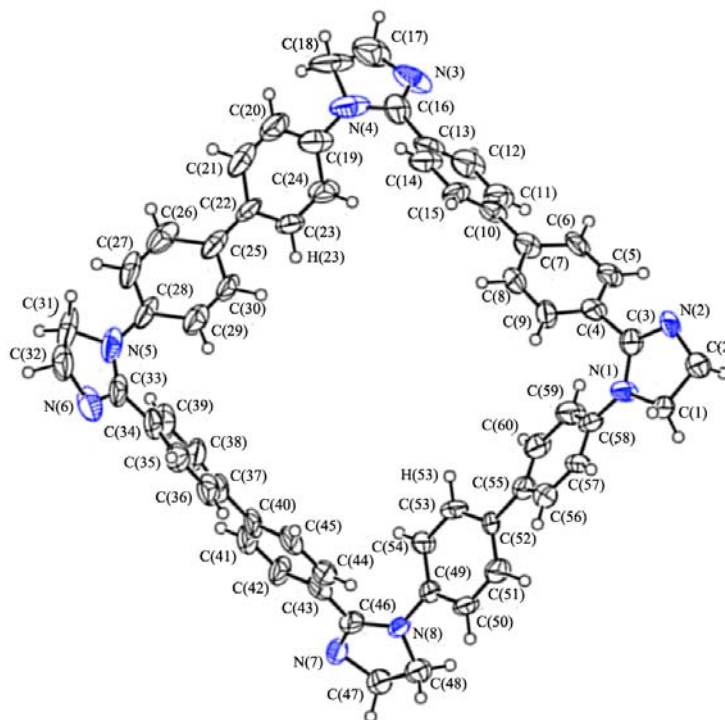


Table S2 The selected bond lengths (Å) in **3b**

N(1)-C(3)	1.407(6)	N(2)-C(3)	1.285(5)
C(3)-C(4)	1.517(6)	N(3)-C(16)	1.250(8)
N(4)-C(16)	1.388(8)	C(13)-C(16)	1.534(8)
N(5)-C(33)	1.361(7)	N(6)-C(33)	1.265(7)
C(33)-C(34)	1.493(8)	N(7)-C(46)	1.248(5)
N(8)-C(46)	1.385(6)	C(43)-C(46)	1.452(6)

Table S3 The twisted angles (degree) in **3b**

N(1)-C(3)-C(4)-C(9)	40.1(7)	C(3)-N(1)-C(58)-C(59)	24.1(8)
N(5)-C(33)-C(34)-C(39)	-31.3(7)	C(8)-C(7)-C(10)-C(15)	37.1(7)
C(14)-C(13)-C(16)-N(4)	-33.6(8)	C(16)-N(4)-C(19)-N(24)	-14.1(10)
C(23)-C(22)-C(25)-C(30)	37.9(8)	C(33)-N(5)-C(28)-C(29)	-12.4(9)
C(38)-C(37)-C(40)-C(41)	-29.2(7)	C(44)-C(43)-C(46)-N(8)	-30.4(8)
C(46)-N(8)-C(49)-C(54)	-28.6(8)	C(53)-C(52)-C(55)-C(60)	-34.0(8)

V. Photophysical properties of **3**

The absorption and emission spectra (excited at 337 nm) of the imidazoline-containing macrocycles **3** were recorded in toluene (5 μ M) at room temperature. As shown in Fig. S3, **3a** and **3b** showed the same absorption maximum at 295 nm and emitted at 470 nm and 460 nm, respectively, which indicated that the isopropyl and phenyl groups on the imidazoline ring had little effects on the spectral properties of the backbones.

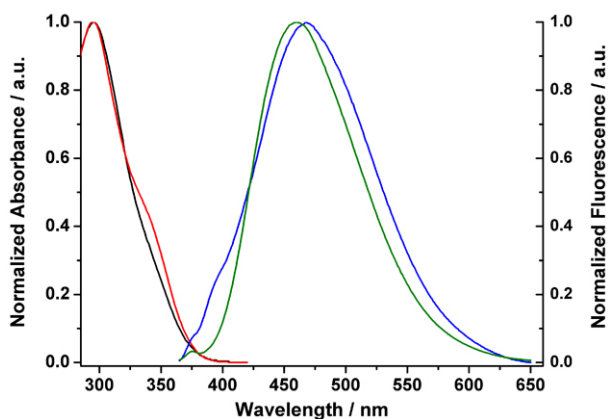


Fig. S3 Normalized absorption (the black line for **3a** and the red line for **3b**) and fluorescence spectra of **3** excited at 337 nm (the blue line for **3a** and the green line for **3b**).

VI. Binding studies of **3** with fullerenes

i. Fluorescent titration experiments

The solutions of macrocycles **3** and fullerenes were freshly prepared before each measurement. The concentration of **3** was 5.0×10^{-6} M or 2.0×10^{-5} M and the concentrations of C₆₀ and C₇₀ were 3.0×10^{-3} M and 1.25×10^{-3} M, respectively. The concentration of C₇₀ was lower due to its lower solubility in toluene.

To a solution of macrocycle **3** (3 mL) in a quartz cell (1 cm thickness) was added variable amounts of fullerene solution using a micro-syringe. The resulting solution was stirred for 1 min and the fluorescence spectra were then recorded (excited at 337 nm). The fluorescence intensities F_{exp} at 470 nm for **3a** and 460 nm for **3b** were collected to calculate the association constants.

Because the competition absorption of C_{60} and C_{70} at the excitation and emission wavelength of **3**, the collected fluorescence intensity F_{exp} was calibrated to F_{cal} using the equation shown below:⁴

$$F_{\text{cal}} = F_{\text{exp}} \times \frac{1 - e^{-\varepsilon_1 C_1 l}}{\varepsilon_1 C_1} \times \frac{\varepsilon_1 C_1 + \varepsilon_2 C_2}{1 - e^{-(\varepsilon_1 C_1 + \varepsilon_2 C_2) l}} \times \frac{\varepsilon_3 C_3 l}{1 - e^{-\varepsilon_3 C_3 l}} \quad (1)$$

Where C_1 and C_2 are the concentration of **3** and fullerenes, and ε_1 and ε_2 are the molar extinction coefficients of **3** and fullerenes at the excitation wavelength ($\lambda_{\text{ex}} = 337$ nm); C_3 and ε_3 are the concentration and molar extinction coefficient of fullerenes at the emission wavelength of **3** (470 nm for **3a** and 460 nm for **3b**); l is the thickness of the cell. The results are summarized in Table S4.

Table S4 Photophysical data for the fluorescence calibration^a

1	ε (3) at λ_{ex}	ε (C_{60}) at λ_{ex}	ε (C_{70}) at λ_{ex}	λ_{em}	ε (C_{60}) at λ_{em}	ε (C_{70}) at λ_{em}
3a	23000	59600	33000	470 nm	600	21600
3b	38000	59600	33000	460 nm	600	18400

^a **3a** and **3b** were both excited at 337 nm in toluene.

The apparent association constant K was determined by the nonlinear curve fitting method⁵ (eqn (2)). c_{H} and c_{G} are the concentrations of macrocycles **3** and fullerenes C_{60} or C_{70} , respectively. F_0 is the fluorescence intensity of **3** before the addition of fullerenes. F_{lim} is the lowest value that the fluorescence intensity can reach after the addition of fullerenes and can be left as a floating parameter in the analysis if it cannot be determined accurately. K can thus be obtained by the nonlinear least squares analysis of F_{cal} versus c_{G} .

$$F_{\text{cal}} = F_0 + \frac{F_{\text{lim}} - F_0}{2} \left\{ 1 + \frac{c_{\text{G}}}{c_{\text{H}}} + \frac{1}{Kc_{\text{H}}} - \left[\left(1 + \frac{c_{\text{G}}}{c_{\text{H}}} + \frac{1}{Kc_{\text{H}}} \right)^2 - 4 \frac{c_{\text{G}}}{c_{\text{H}}} \right]^{1/2} \right\} \quad (2)$$

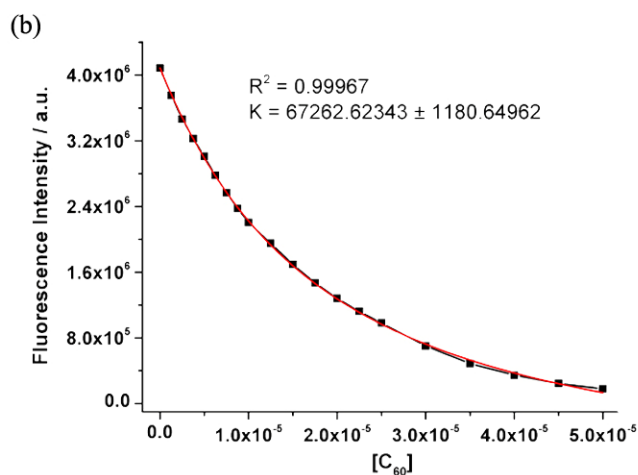
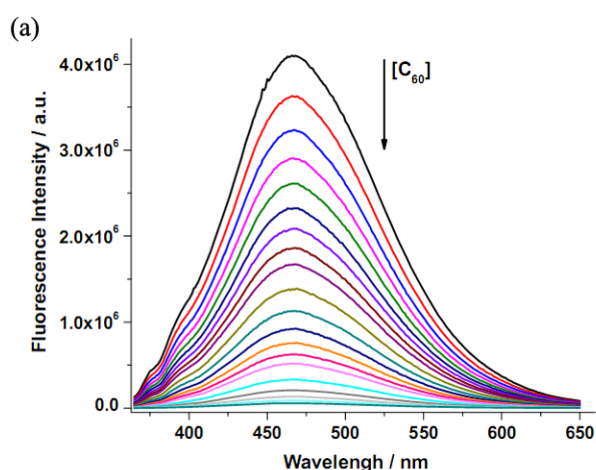


Fig. S4 (a) Fluorescence spectra ($\lambda_{\text{ex}} = 337 \text{ nm}$) of the toluene solution of **3a** ($5.0 \times 10^{-6} \text{ mol}\cdot\text{dm}^{-3}$) in the presence of C_{60} (From top to bottom: 0.0, 1.25, 2.5, 3.75, 5.0, 6.25, 7.5, 8.75, 10.0, 12.5, 15.0, 17.5, 20.0, 22.5, 25.0, 30.0, 35.0, 40.0, 45.0, and 50.0 ($\times 10^{-6} \text{ mol}\cdot\text{dm}^{-3}$)) at 25 °C. (b) The association constant K obtained by nonlinear curve fitting (eqn (2)) at the emission of 470 nm.

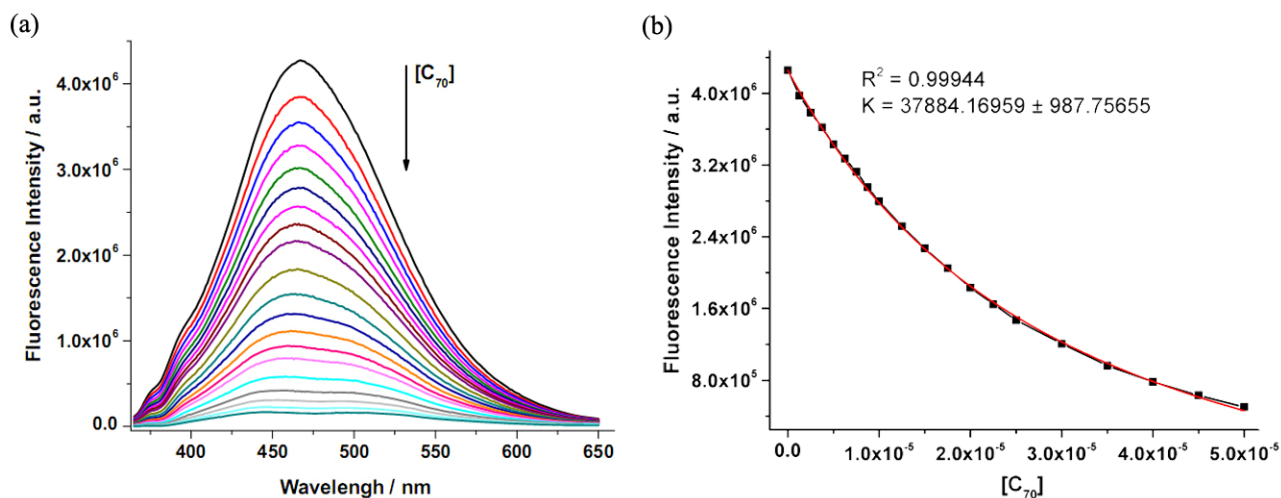


Fig. S5 (a) Fluorescence spectra ($\lambda_{\text{ex}} = 337 \text{ nm}$) of the toluene solution of **3a** ($5.0 \times 10^{-6} \text{ mol}\cdot\text{dm}^{-3}$) in the presence of C_{70} (From top to bottom: 0.0, 1.25, 2.5, 3.75, 5.0, 6.25, 7.5, 8.75, 10.0, 12.5, 15.0, 17.5, 20.0, 22.5, 25.0, 30.0, 35.0, 40.0, 45.0, and 50.0 ($\times 10^{-6} \text{ mol}\cdot\text{dm}^{-3}$)) at 25 °C. (b) The association constant K obtained by nonlinear curve fitting (eqn (2)) at the emission of 470 nm.

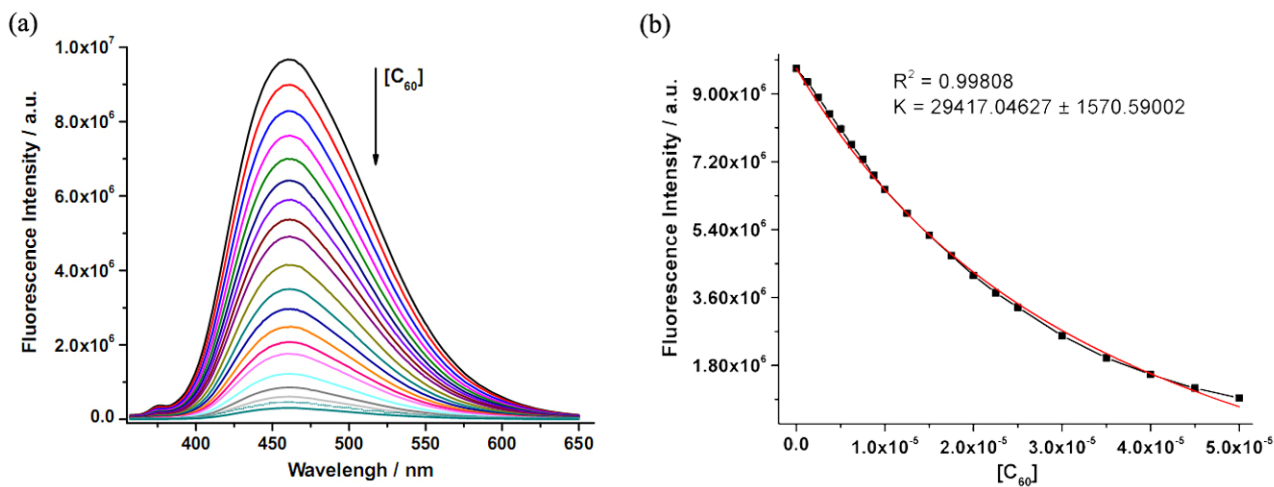


Fig. S6 (a) Fluorescence spectra ($\lambda_{\text{ex}} = 337 \text{ nm}$) of the toluene solution of **3b** ($5.0 \times 10^{-6} \text{ mol}\cdot\text{dm}^{-3}$) in the presence of C_{60} (From top to bottom: 0.0, 1.25, 2.5, 3.75, 5.0, 6.25, 7.5, 8.75, 10.0, 12.5, 15.0, 17.5, 20.0, 22.5, 25.0, 30.0, 35.0, 40.0, 45.0, and 50.0 ($\times 10^{-6} \text{ mol}\cdot\text{dm}^{-3}$)) at 25 °C. (b) The association constant K obtained by nonlinear curve fitting (eqn (2)) at the emission of 460 nm.

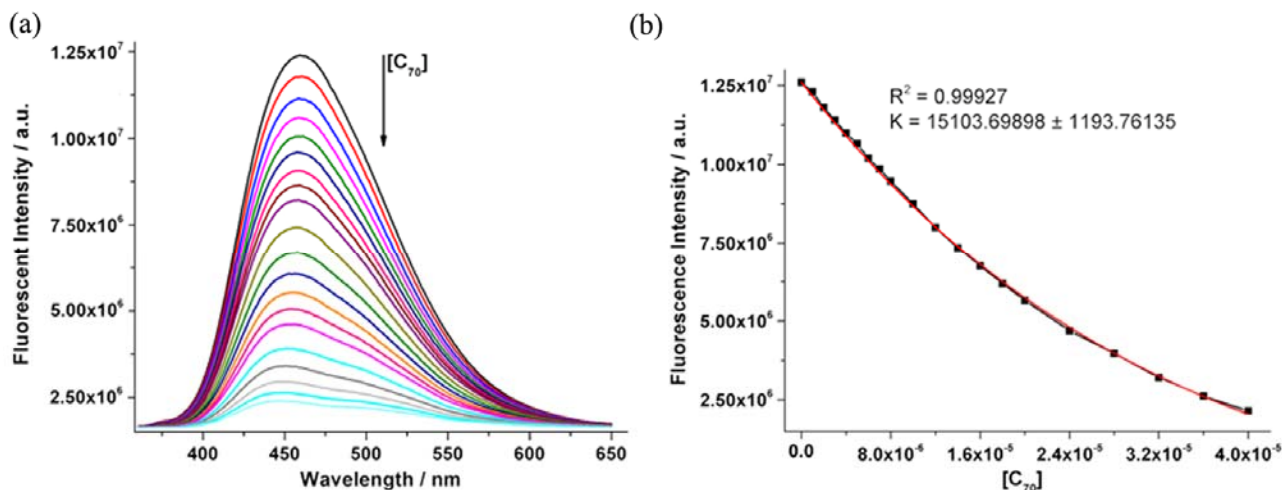


Fig. S7 (a) Fluorescence spectra ($\lambda_{\text{ex}} = 337 \text{ nm}$) of the toluene solution of **3b** ($2.0 \times 10^{-5} \text{ mol}\cdot\text{dm}^{-3}$) in the presence of C_{70} (From top to bottom: 0.0, 1.0, 2.0, 3.0, 4.0, 5.0, 6.0, 7.0, 8.0, 10.0, 12.0, 14.0, 16.0, 18.0, 20.0, 24.0, 28.0, 32.0, 36.0 and $40.0 (\times 10^{-6} \text{ mol}\cdot\text{dm}^{-3})$) at 25°C . (b) The association constant K obtained by nonlinear curve fitting (eqn (2)) at the emission of 460 nm.

ii. The Job plot experiments

The solution of macrocycles **3** and fullerenes in toluene were prepared with different molar ratios (**3**/fullerenes: 10:0, 9:1, 8:2, 7:3, 6:4, 5:5, 4:6, 3:7, 2:8, 1:9, 0:10), keeping the total concentration in $1.0 \times 10^{-5} \text{ M}$. Then the fluorescence spectra were recorded with excitation at 337 nm.

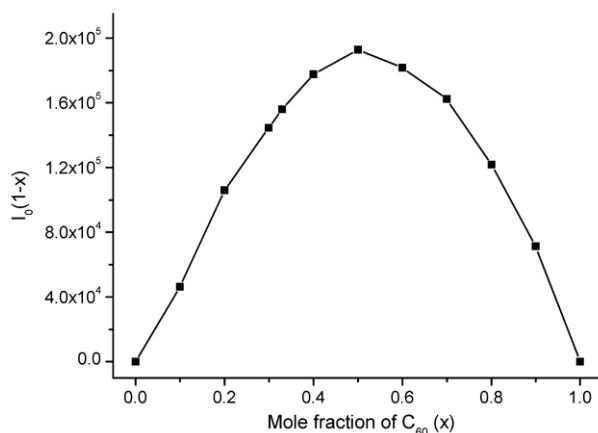


Fig. S8 Job's Plot of **3a** with C_{60} in toluene measured at 470 nm. ($x = [C_{60}]/([C_{60}] + [3a])$, $[C_{60}] + [3a] = 10 \mu\text{M}$).

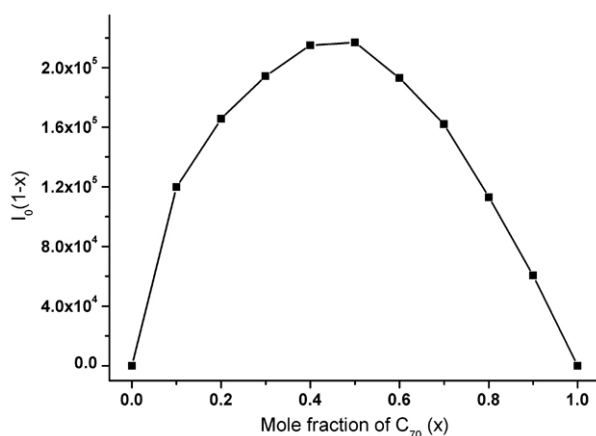


Fig. S9 Job's Plot of **3a** with C_{70} in toluene measured at 470 nm. ($x = [C_{70}]/([C_{70}] + [3a])$, $[C_{70}] + [3a] = 10 \mu\text{M}$).

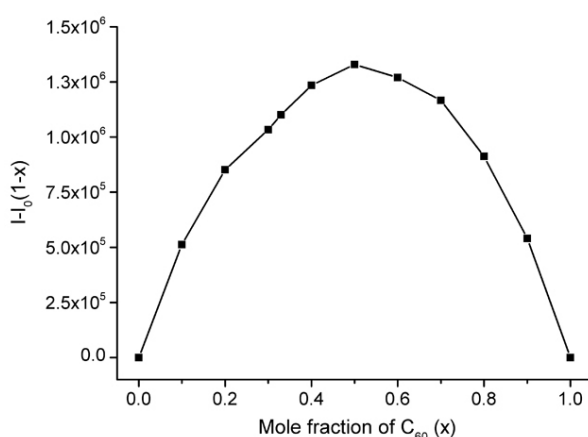


Fig. S10 Job's Plot of **3b** with C_{60} in toluene measured at 460 nm. ($x = [C_{60}]/([C_{60}] + [3b])$, $[C_{60}] + [3b] = 10 \mu\text{M}$).

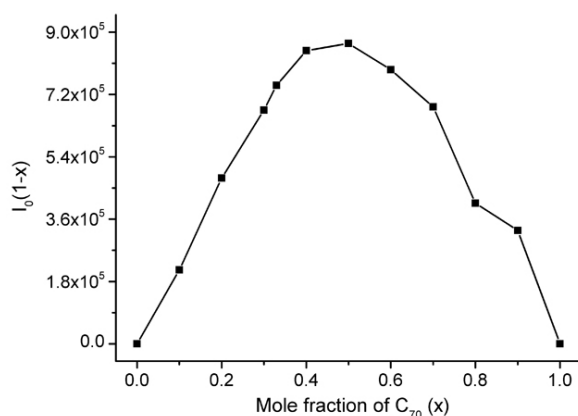


Fig. S11 Job's Plot of **3b** with C_{70} in toluene measured at 460 nm. ($x = [C_{70}]/([C_{70}] + [3b])$, $[C_{70}] + [3b] = 10 \mu\text{M}$).

iii. Fluorescence lifetime measurements

Fluorescence measurements were performed using a Single Photon Counting Controller FluoroHub-B. A 5.0×10^{-6} M toluene solution of macrocycles **3** (in the absence or presence of

C_{60}/C_{70}) was excited at 370 nm using a NanoLED-370 as the excitation light source, and the emitted photons were detected by a TBX detector connected to a TBX-PS power supply. Emission decays were monitored at 470 nm for **3a** and 460 nm for **3b**, respectively. The fluorescence decay data were analyzed using DAS-6 Fluorescence Decay Analysis software and were fitted to biexponential decay function.

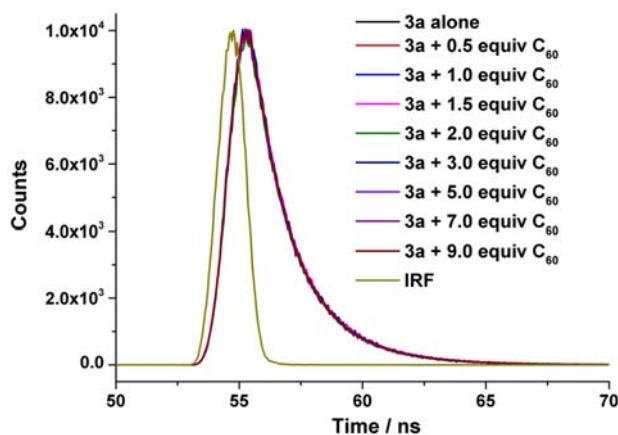


Fig. S12 Fluorescence lifetime measurements ($\lambda_{\text{ex}} = 370$ nm, $\lambda_{\text{em}} = 470$ nm) of the toluene solution of **3a** (5.0×10^{-6} mol·dm $^{-3}$) in the presence of different amounts of C_{60} at 25 °C. The dark yellow profile on the extreme left represents the instrument response function (IRF). Time calibration = 5.49×10^{-11} sec/ch.

Table S5 Fluorescence lifetimes of **3a** in the presence of different amounts of C_{60}

$[C_{60}]$ μM	τ_1 (ns)	τ_2 (ns)	α_1 (%)	α_2 (%)	avg τ (ns)	χ^2
0.0	1.02	2.15	53	47	1.55	0.99
2.5	1.13	2.24	60	40	1.57	1.00
5.0	1.22	2.30	64	36	1.60	1.00
7.5	1.17	2.26	62	38	1.59	0.99
10.0	1.14	2.25	60	40	1.58	1.00
15.0	1.18	2.28	63	37	1.59	0.99
25.0	1.21	2.29	64	36	1.60	1.00
35.0	1.21	2.33	65	35	1.60	1.00
45.0	1.10	2.21	58	42	1.57	0.99

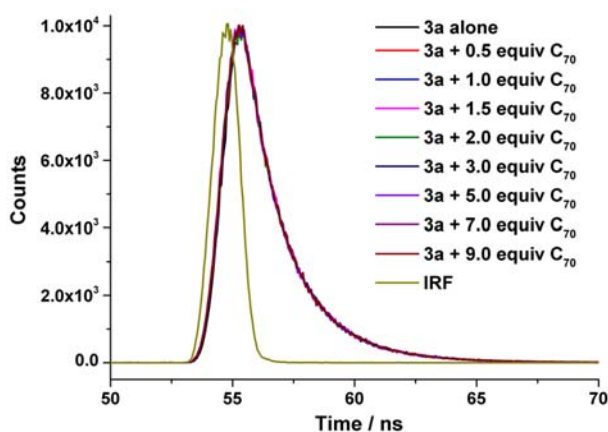


Fig. S13 Fluorescence lifetime measurements ($\lambda_{\text{ex}} = 370$ nm, $\lambda_{\text{em}} = 470$ nm) of the toluene solution of **3a** (5.0

$\times 10^{-6} \text{ mol}\cdot\text{dm}^{-3}$) in the presence of different amounts of C_{70} at 25 °C. The dark yellow profile on the extreme left represents the instrument response function (IRF). Time calibration = $5.49 \times 10^{-11} \text{ sec/ch}$.

Table S6 Fluorescence lifetimes of **3a** in the presence of different amounts of C_{70}

$[\text{C}_{70}] \mu\text{M}$	τ_1 (ns)	τ_2 (ns)	α_1 (%)	α_2 (%)	avg τ (ns)	χ^2
0.0	1.12	2.23	58	42	1.59	0.99
2.5	1.20	2.33	65	35	1.60	1.00
5.0	1.20	2.33	65	35	1.60	1.00
7.5	1.28	2.43	71	29	1.61	1.00
10.0	1.26	2.38	68	32	1.61	0.99
15.0	1.23	2.39	68	32	1.60	1.01
25.0	1.25	2.38	69	31	1.60	1.01
35.0	1.27	2.44	71	29	1.61	0.99
45.0	1.30	2.49	73	27	1.62	1.00

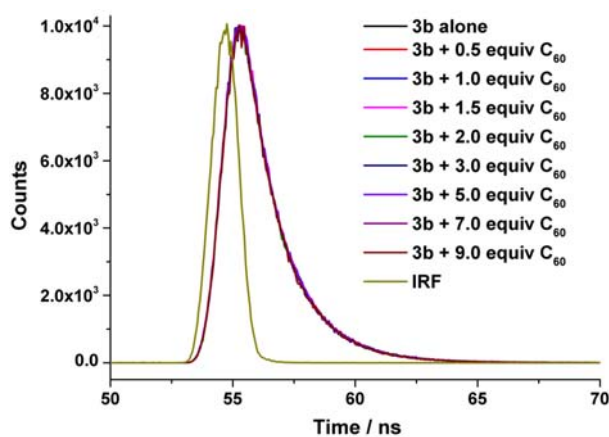


Fig. S14 Fluorescence lifetime measurements ($\lambda_{\text{ex}} = 370 \text{ nm}$, $\lambda_{\text{em}} = 460 \text{ nm}$) of the toluene solution of **3b** ($5.0 \times 10^{-6} \text{ mol}\cdot\text{dm}^{-3}$) in the presence of different amounts of C_{60} at 25 °C. The dark yellow profile on the extreme left represents the instrument response function (IRF). Time calibration = $5.49 \times 10^{-11} \text{ sec/ch}$.

Table S7 Fluorescence lifetimes of **3b** in the presence of different amounts of C_{60}

$[\text{C}_{60}] \mu\text{M}$	τ_1 (ns)	τ_2 (ns)	α_1 (%)	α_2 (%)	avg τ (ns)	χ^2
0.0	0.68	1.65	26	74	1.40	1.00
2.5	0.71	1.67	28	72	1.40	0.99
5.0	0.91	1.72	35	65	1.44	1.00
7.5	0.97	1.74	39	61	1.44	0.99
10.0	0.74	1.68	30	70	1.40	1.02
15.0	0.79	1.69	30	70	1.42	0.99
25.0	0.88	1.70	32	68	1.44	1.02
35.0	1.03	1.78	43	57	1.45	1.00
45.0	0.85	1.71	35	65	1.41	1.01

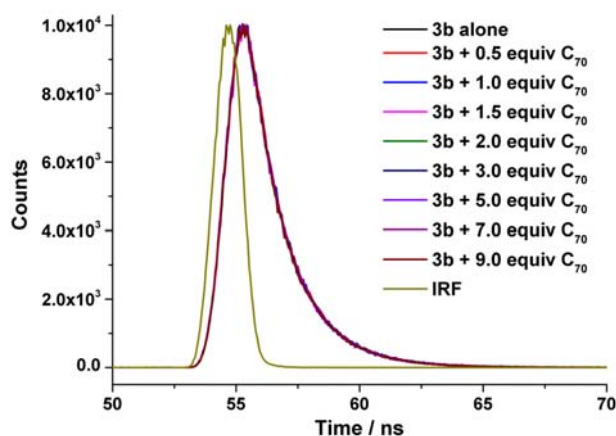


Fig. S15 Fluorescence lifetime measurements ($\lambda_{\text{ex}} = 370$ nm, $\lambda_{\text{em}} = 460$ nm) of the toluene solution of **3b** (5.0×10^{-6} mol·dm $^{-3}$) in the presence of different amounts of C $_{70}$ at 25 °C. The dark yellow profile on the extreme left represents the instrument response function (IRF). Time calibration = 5.49×10^{-11} sec/ch.

Table S8 Fluorescence lifetimes of **3b** in the presence of different amounts of C $_{70}$

[C $_{70}$] μM	τ_1 (ns)	τ_2 (ns)	α_1 (%)	α_2 (%)	avg τ (ns)	χ^2
0.0	0.68	1.63	24	76	1.40	1.00
2.5	1.02	1.77	42	58	1.46	0.99
5.0	1.13	1.85	53	47	1.47	0.99
7.5	1.17	1.85	54	46	1.48	1.02
10.0	0.98	1.79	45	55	1.43	1.02
15.0	1.11	1.84	52	48	1.46	1.02
25.0	0.58	1.62	26	74	1.35	1.01
35.0	0.54	1.62	23	77	1.37	1.00
45.0	0.99	1.75	39	61	1.45	0.99

VII. References

- 1 M. J. McKennon and A. I. Meyers, *J. Org. Chem.*, 1993, **58**, 3568.
- 2 J. Munch-Petersen, *Org. Synth.*, 1953, **33**, 53.
- 3 (a) N. A. Boland, M. Casey, S. J. Hynes, J. W. Matthews and M. P. Smyth, *J. Org. Chem.*, 2002, **67**, 3919; (b) K. Ma and J. You, *Chem. Eur. J.*, 2007, **13**, 1863; (c) L. Yan, Z. Wang, M.-T. Chen, N. Wu, J. Lan, X. Gao, J. You, H.-M. Gau and C.-T. Chen, *Chem. Eur. J.*, 2008, **14**, 11601; (d) L. Yan, Y. Xue, G. Gao, J. Lan, F. Yang, X. Su and J. You, *Chem. Eur. J.*, 2010, **16**, 2250.
- 4 M. Zheng, F. Bai, F. Li, Y. Li and D. Zhu, *J. Appl. Polym. Sci.*, 1998, **70**, 599.
- 5 D. K. Ryan and J. H. Weber, *Anal. Chem.*, 1982, **54**, 986.

VIII. Copies of ^1H and ^{13}C NMR spectra

