Supporting Information

Visible and Near-infrared Photoluminescence in A Supramolecular Complex Constructed by Cycloparaphenylene Nanoring and Erbium Metallofullerene

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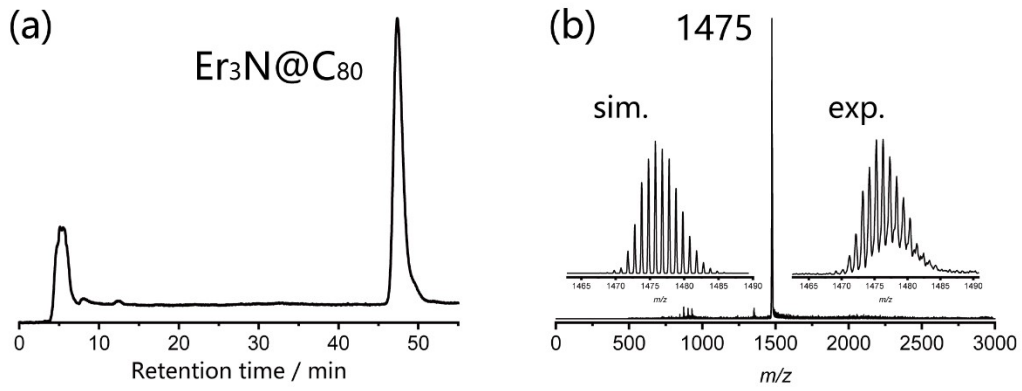

Figure S1. (a) HPLC chromatograms of $Er_3N@C_{80}$ with a 20×250 mm Buckyprep column, 12 mL/min flow rate with toluene as eluent phase. (b) MALDI-TOF-MS spectra of $Er_3N@C_{80}$; the insets show the isotopic distributions.

Job's plot measurement.

A UV-Vis spectroscopic titration was carried out in toluene. The absorption spectrum of $Er_3N@C_{80}$ changed on addition of [12]CPP (Figure S2a). The intensity of the absorption maximum at 340 nm gradually increased with an isosbestic point of 314 nm and 382 nm. This is attributed to the interaction between the fullerene cage and [12]CPP.

The complexation stoichiometry was determined by a Job's plot based on the absorption change at 340 nm. A solution of $Er_3N@C_{80}$ and [12]CPP in toluene was prepared in 11 different ratio [$Er_3N@C_{80}$/($Er_3N@C_{80}$ + [12]CPP) = 0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8 0.9, 1] of samples at a fixed overall concentration of 1.5×10^{-5} M. Absorption measurements were performed at 25 °C. The continuous variation plot with a maximum value of 0.5, provided evidence for the formation of a 1:1 complex of $Er_3N@C_{80}$ and [12]CPP (Figure S2b).

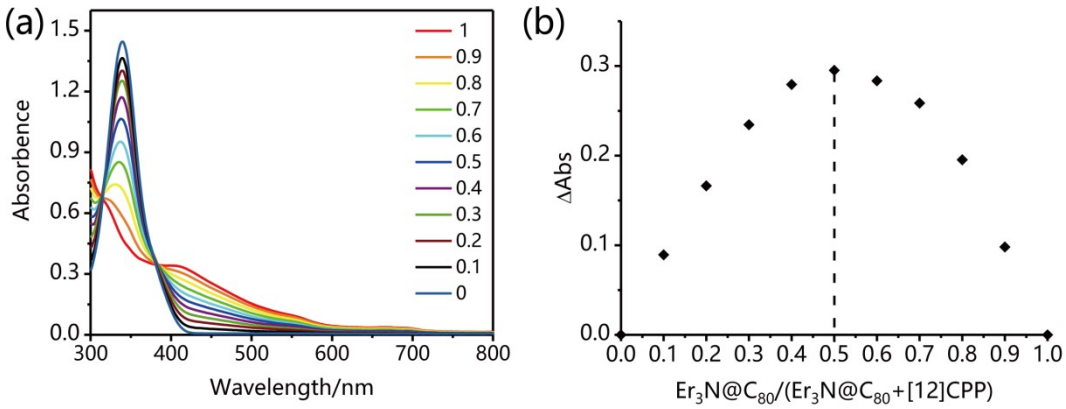

Figure S2. (a) UV-vis absorption spectra of $Er_3N@C_{80}$ after adding [12]CPP in toluene solution. (b) The Job's plot of $Er_3N@C_{80}$ and [12]CPP complexation.

Electrochemistry experiment.

Voltammetric measurements were carried out using a CHI 760E Electrochemical Workstation (CH Instrument). The electrolyte used in the experiment is $TBAPF_6$ with concentration of 0.05 M, and the solvent is *o*-DCB. Glassy carbon electrode is used as working electrode, reference electrode is silver electrode and auxiliary electrode is platinum filament. The scan rate is 50 mv/s. The potentials are referred to the $E_{1/2}$ value of the Fc/Fc^+ redox couple measured in the sample solution.

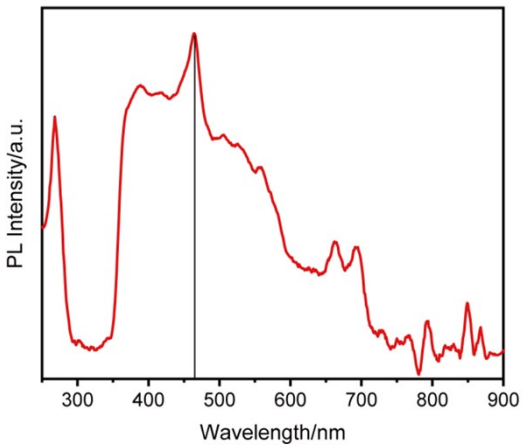

Figure S3. Excitation spectrum of $Er_3N@C_{80}$ in CS_2 at 77 K, with maximum emission intensity at 465 nm.

Fluorescence titration experiment.

To toluene solution of [12]CPP (6.0×10^{-7} M, 2.0 mL) was gradually added 2 μL of toluene solution of $Er_3N@C_{80}$ (6.0×10^{-5} M, 0–26 μL). Photoluminescence measurements were performed at λexc = 365 nm at 25 °C. The binding constants were determined by using the following equation:

$$F / F_0 = (1 + k_n * K_a * M_{[EMF]}) / (1 + K_a * M_{[EMF]})$$

, where F_0 and F are the photoluminescence intensity of [12]CPP in the absence and presence of different concentrations of $M_{[EMF]}$, respectively. On the other hand, k_n is the ratio of the proportionality constant of the complexes to the proportionality constant of the [12]CPP, and K_a is the binding constant of the complexes.

With the addition of $Er_3N@C_{80}$, the photoluminescence intensity of [12] CPP gradually decreased, by monitoring this decrease in photoluminescence at 450 nm, the binding constants (K_a) of [12]CPP with $Er_3N@C_{80}$ was determined to be $(8.35\pm0.91)\times10^5$ M^{-1}.(Figure S3)

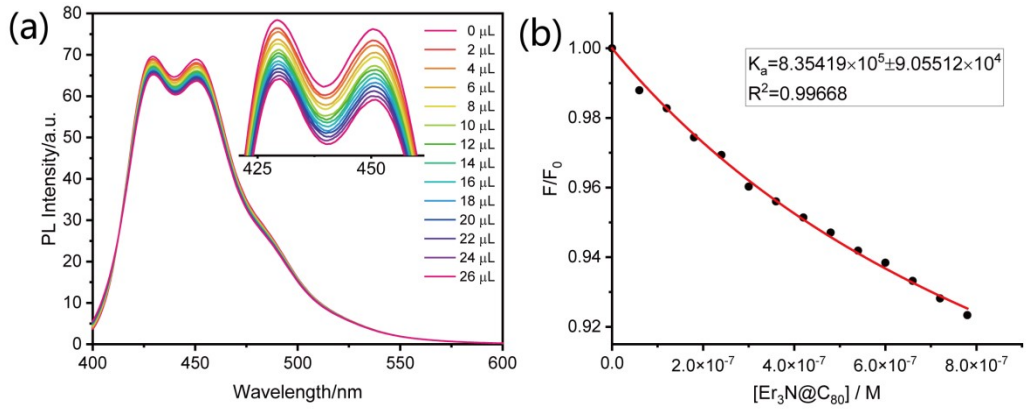

Figure S4. (a) Photoluminescence spectra of [12]CPP in the presence of $Er_3N@C_{80}$ (0.0–1.3 equiv) in toluene solution at 25 °C. The insets show the enlarged spectra from 420 to 460 nm. (b) Photoluminescence titration plot for determination of the binding constant of [12]CPP in the presence of various amounts of metallofullerenes.

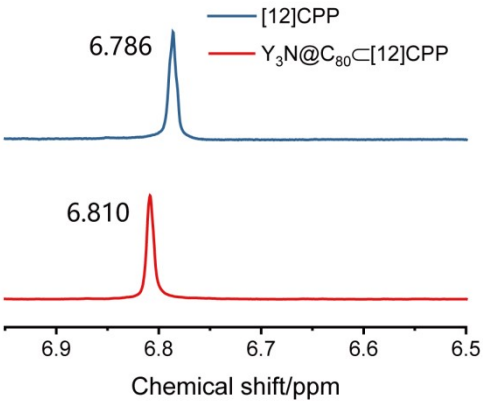

Figure S5. ^{1}H NMR for [12]CPP and $Y_3N@C_{80}\subset$[12]CPP in CS_2 solution at 298 K with [D_6]acetone as an internal lock.

Cartesian coordinates for optimized $Er_3N@C_{80}$ at B3LYP/6-31G(d)~SDD level of theory.

C	3.56168000	-2.14755700	-1.11822300
C	3.96801100	-1.75594700	0.26109600
C	4.15421900	-0.29920900	0.23517800
C	3.92295000	0.18421400	-1.10240500
C	3.53827600	-0.93019100	-1.92426700
C	3.49258200	1.53899800	-1.38807800
C	3.29531900	2.42912400	-0.28906000
C	3.43822200	1.94694000	1.05394800
C	3.81251700	0.58606800	1.33467000
C	2.28412800	3.47186700	-0.30441600
C	1.78703300	3.62994700	1.05945300
C	2.49719600	2.65707700	1.87723000
C	2.69250700	1.75050500	-2.53758500
C	2.26457300	0.64251000	-3.35011800
C	2.63144700	-0.70226100	-3.03288200
C	1.64882000	2.75796100	-2.54422800
C	1.42090700	3.65970400	-1.44567000

C	0.57905300	2.24812200	-3.37112100
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C	-0.46178900	4.31334000	0.18828000
C	0.05106800	4.12263900	-1.19803400
C	-0.18135000	3.30767500	2.45182700
C	0.54833800	2.37901200	3.29487300
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Er	1.73617500	-1.07317400	-0.01599600
Er	-1.82064600	-0.92527300	-0.01847800
Er	0.08241200	2.03512100	-0.01690200
N	-0.00157100	-0.00395600	0.05868300

Cartesian coordinates for optimized Er3N@C80⊂[12]CPP at B3LYP/6-31G(d)~SDD level of theory.

C	-7.80019100	-1.32527300	0.77162500
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C	-0.72390600	7.76474700	1.52416100
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C	1.36217400	7.55091700	0.28995800
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H	-1.61011400	-7.19976200	-2.31280800
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C	-0.27752600	2.47091500	-3.21593200
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C	0.84186700	1.62046400	-3.45739000
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C	0.60767400	-1.98528300	-3.36859500
C	1.42537000	-0.80799800	-3.49840600
C	-3.43314500	-2.61526800	-0.57495600

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C	1.07703900	-3.99626000	0.41566800
C	2.86816200	0.75380600	-2.28168100
C	-3.62468500	-0.74490800	2.48078000
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C	-2.77763400	-1.84090500	2.86916900
C	2.04530500	1.86087900	-2.68289600
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C	0.75296500	3.98942700	0.01150200
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C	-2.81531800	2.77370100	1.75767000

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C	-1.33461600	1.96759300	3.52284500
C	-1.62384400	2.94915600	2.53779000
C	-0.52104100	3.63466600	1.93129500
C	3.00672100	-2.32466500	0.46113900
C	3.48770600	-1.34140300	-0.48035200
C	3.73208500	0.01768300	-0.08574300
C	3.51661800	1.09372400	-1.04030200
C	3.13702100	2.46616900	-0.66241100
C	-1.58304700	-1.62513400	3.62099900
C	-1.31007400	-0.29870200	4.05343900
C	0.04072800	0.20062000	4.14718700
C	0.02291100	1.60578300	3.83237400
C	2.83925000	2.72577200	0.76068500
C	1.65679700	3.51564800	1.05620500
C	0.83823800	3.28365900	2.23599000
C	1.11713800	2.22169600	3.15706600
C	0.88951200	-3.77462100	1.86515000
C	-0.48764600	-3.60503700	2.40632800
C	-0.45699100	-2.50481100	3.35878200
C	2.76741900	-1.99965100	1.82376400
C	1.70710500	-2.72935100	2.50491900
C	0.88230000	-1.98787400	3.42937700
C	1.14990100	-0.61314400	3.80001100
C	2.26947400	1.42561100	2.88950400
C	2.28750600	0.02611200	3.21506800
C	3.08008400	-0.65934400	2.23263100
C	3.54927200	0.32719000	1.28860600
C	3.06407200	1.63811200	1.69149000

Er	1.13027400	1.34555500	-0.21899500
Er	-2.28883300	0.40011500	-0.50264200
Er	0.03797400	-1.85650700	0.84002600
N	-0.37767600	0.01267300	0.12858800