Supporting Information

for

A self-assembled white-light-emitting system in aqueous medium based on macrocyclic amphiphile

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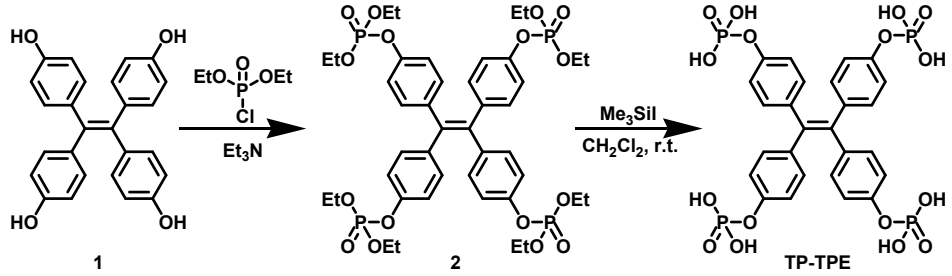
General methods and materials

All the reagents and solvents were commercially available and used as received unless otherwise specified purification. 4,7-Di(2-thienyl)-2,1,3-benzothiadiazole (**DBT**) was purchased from TCI. 5,11,17,23-Tetraguanidinium-25,26,27,28-tetradodecyloxy-calix[4]arene (**GC4A**) was synthesized according to the previous literature.[1] 1-(4-(Dodecyloxy)phenyl)guanidinium (**Gua-12C**), the monomer of **GC4A**, was synthesized and purified according to the procedure reported previously.[2] The HEPES buffer solution of pH 6.0 was prepared by dissolving 2.38 g of 2-[4-(2-hydroxyethyl)piperazin-1-yl]ethanesulfonic acid (HEPES) in approximate 900 mL double-distilled water. Titrate to pH 6.0 at the lab temperature of 25 °C with NaOH and make up volume to 1000 ml with double-distilled water. The pH value of the buffer solution was then verified on a pH-meter calibrated with two standard buffer solutions.

NMR data were recorded on a Bruker AV400 spectrometer. High resolution mass spectra (HRMS) were performed on a VG ZAB-HS (ESI) and a Varian 7.0T FTMS (MALDI-TOF). UV-Vis spectra were recorded in a quartz cell (light path 10 mm) on a Shimadzu UV-3600 spectrophotometer equipped with a PTC-348WI temperature controller. Steady-state fluorescence spectra were recorded in a conventional quartz cell (light path 10 mm) on a Varian Cary Eclipse equipped with a Varian Cary single-cell peltier accessory to control temperature. The fluorescence lifetimes were measured by time-correlated single photon counting on a FLS920 instrument (Edinburg Instruments Ltd., Livingstone, UK) with a H2 pulse lamp. The sample solutions for dynamic light scattering (DLS) measurements were examined on a laser light scattering spectrometer (NanoBrook 173plus) equipped with a digital correlator at 659 nm at a scattering angle of 90°. Scanning electron microscopy (SEM) images were recorded on a JSM-7500F scanning electron microscope. The sample for SEM measurement was prepared by dropping the solution onto a silicon wafer. The wafer was then air-dried.

Preparation of GC4A nanoparticles. GC4A and **PEG-C12** (molar ratio 10:1) were dissolved in methanol. After removal of methanol under reduced pressure, the residue was rehydrated in HEPES buffer (10 mM, pH = 6.0) by sonication at 80 °C.

Synthesis of TP-TPE

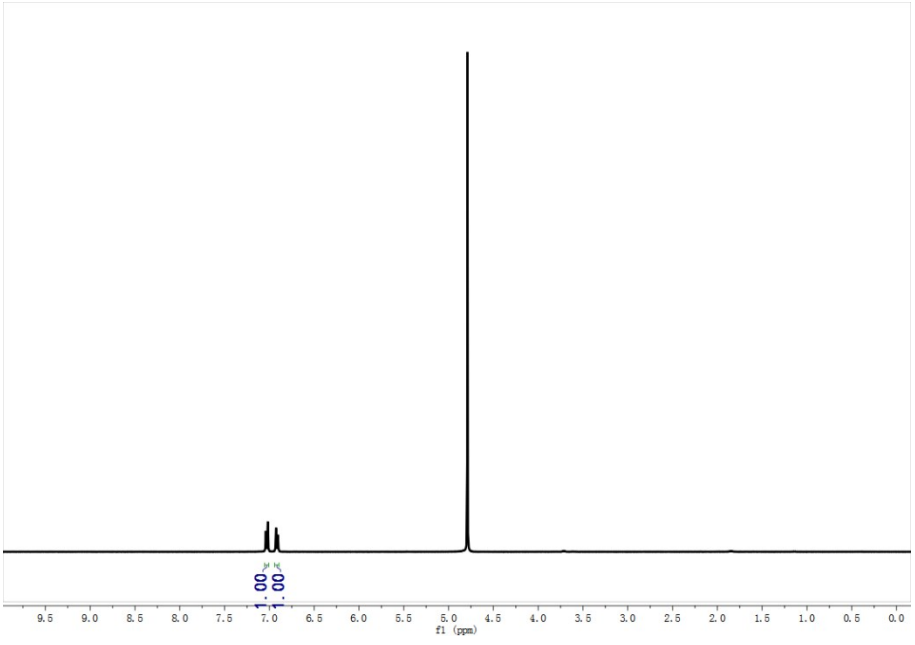


Scheme S1. Synthetic route of **TP-TPE.**

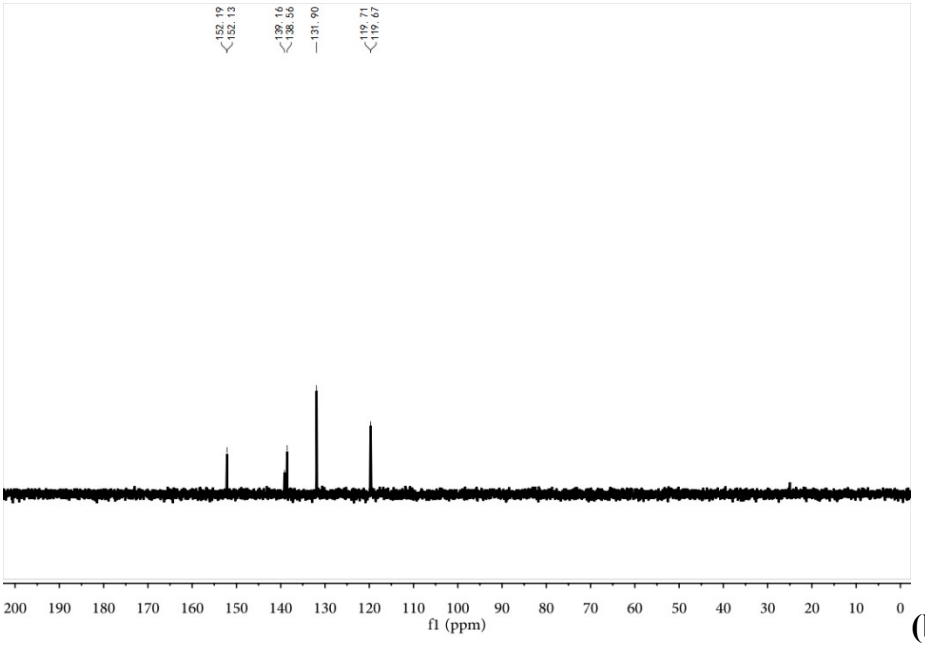
4,4',4",4"'-(Ethene-1,1,2,2-tetrayl)tetraphenol **1** was synthesized and purified according to the procedure reported previously.[3]

Ethene-1,1,2,2-tetrayltetra(benzene-4,1-diyl) octaethyl tetrakis(phosphate) (2). In a single neck round bottom flask 100 mg (0.25 mmol) compound **1** was taken in 5 mL dry chloroform under an argon atmosphere. Triethyl amine (0.72 μL, 10 mmol) and diethylchlorophosphate (0.72 mL, 5 mmol) were added slowly one after another into a stirred solution of **1** at 0 °C. The reaction mixture was brought to room temperature and stirred overnight. The reaction mixture was then concentrated under reduced pressure. The residue was re-dissolved in dichloromethane, washed with brine followed by water and the collected organic layer was dried over sodium sulphate and filtered. The organic solvent was removed under reduced pressure to afford the crude product, which was purified by column chromatography to obtain the desired **2** (102 mg, 42%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.99 (d, J = 1.8 Hz, 4H), 4.23 (qd, J = 7.1, 2.0 Hz, 4H), 1.37 (td, J = 7.1, 1.1 Hz, 6H).

Ethene-1,1,2,2-tetrayltetrakis(benzene-4,1-diyl) tetra(dihydrogen phosphate) (TP-TPE). Compound **2** (100 mg, 0.11 mmol) was taken in 2 mL dry dichloromethane under an argon atmosphere. To it trimethylsilyl iodide (0.15 mL, 1.1 mmol) was added slowly at 0 °C. The reaction mixture was brought to room temperature and stirred for 2 h. The reaction mixture was then concentrated under reduced pressure and the crude residue was directly subjected to column chromatography to afford pure **TP-TPE** (68 mg, 90%). ^{1}H NMR (400 MHz, D_2O/NaOD) δ 7.06-7.00 (m, 8H), 6.95-6.88 (m, 8H); ^{13}C NMR (100 MHz, D_2O/NaOD) δ 152.19, 152.13, 139.16, 138.56, 131.90, 119.71, 119.67; HRMS (ESI-MS): calcd. for $C_{26}H_{23}O_{16}P_4^-$ $[M-H]^-$ 714.9937, found 714.9935.


1.00
1.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

(a)


152.19
152.13
139.16
138.56
131.90
119.71
119.67
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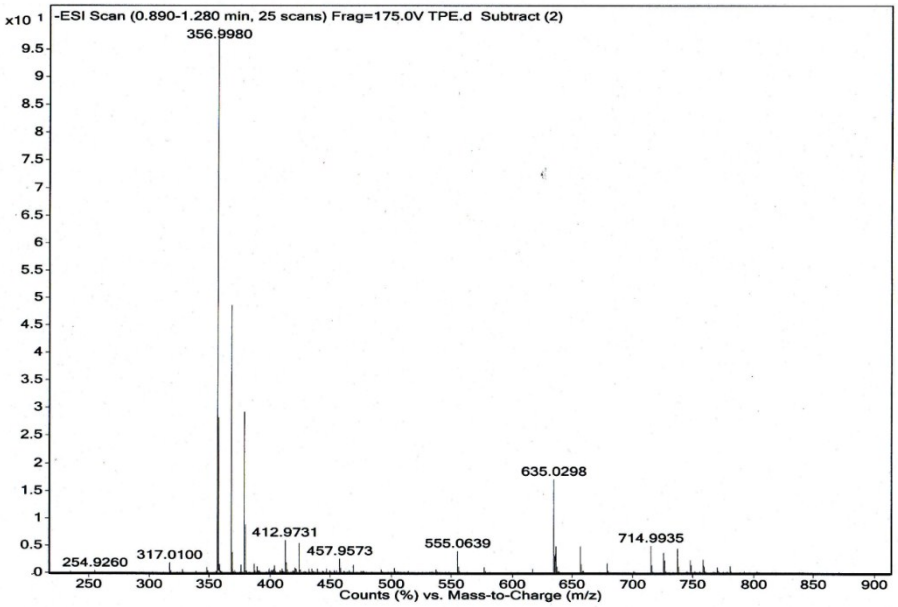
f1 (ppm)

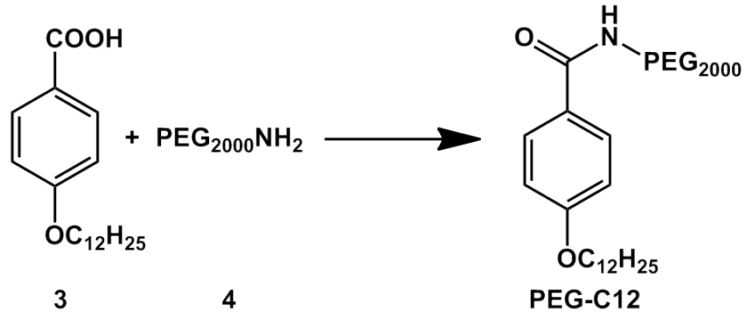
(b)



(c)

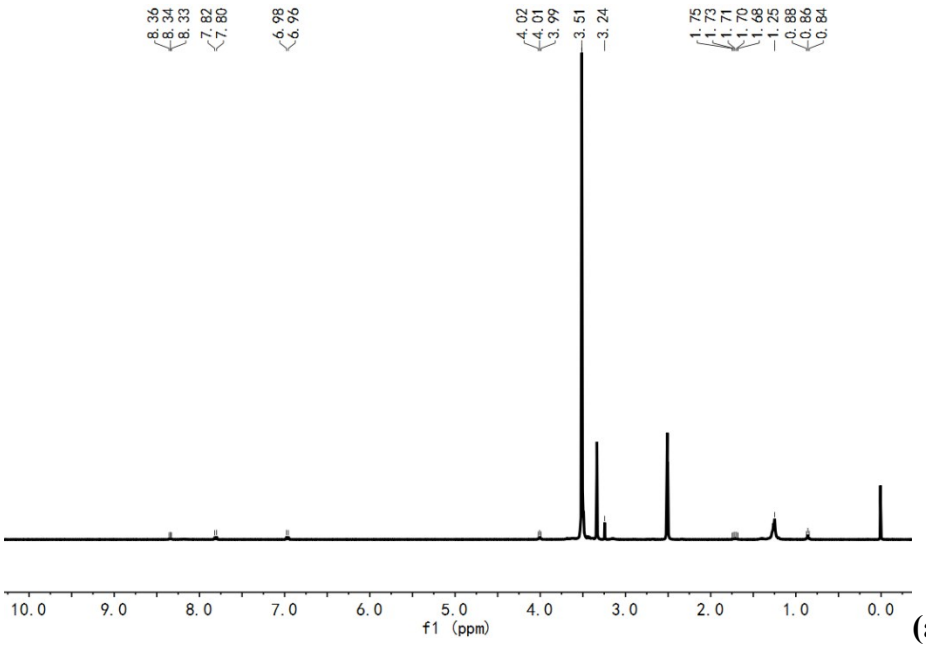
Figure S1. (a) ^{1}H NMR spectrum of **TP-TPE** in D_2O/NaOD; (b) ^{13}C NMR spectrum of **TP-TPE** in D_2O/NaOD; (c) HRMS (ESI-MS) spectrum of **TP-TPE**.

Synthesis of PEG-C12.

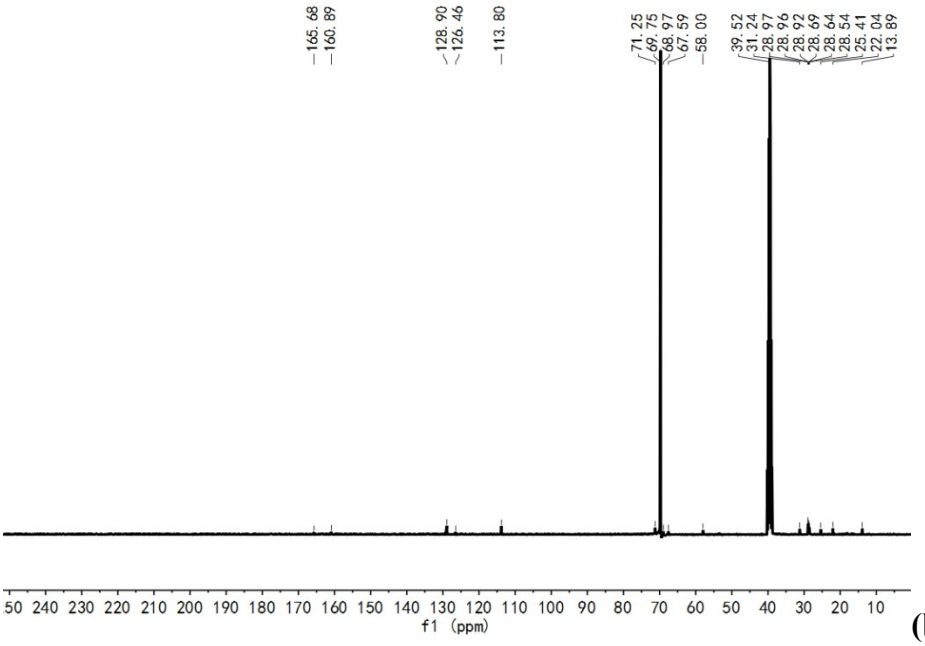


Scheme S2. Synthetic route of **PEG-C12.**

4-(Dodecyloxy)benzamido-terminated methoxy poly(ethylene glycol) (PEG-C12). To a solution of **3** (244 mg, 0.8 mmol) in 10 mL DMF, **4** (200 mg, 0.2 mmol), HOBT (108 mg, 0.8 mmol) and HBTU (303 mg, 0.8 mmol) were added. The solution is then stirred 30 minutes at room temperature under an argon atmosphere, followed by addition of DIPEA (0.26 mL, 1.6 mmol). The mixture was stirred at room temperature for 4h. After addition of 400 mL diethyl ether, the solution was stored in refrigerator for a night. The residue was obtained by centrifugation, followed by purified by dialysis and freeze-drying to give **PEG-C12** as a white solid (213 mg, 93%). ^{1}H NMR (400 MHz, DMSO-d6) δ 8.33 (t, J = 5.6 Hz, 1H), 7.81 (d, J = 8.7 Hz, 2H), 6.96 (d, J = 8.7 Hz, 2H), 4.00 (t, J = 6.5 Hz, 2H), 3.51 (s, 168H), 3.24 (s, 3H), 1.70 (q, J = 6.8 Hz, 2H), 1.25 (m, 18H), 0.86 (m, 3H); ^{13}C NMR (100 MHz, DMSO-d6) δ 165.68, 160.89, 128.90, 126.46, 113.80, 71.25, 69.75, 68.97, 67.59, 58.00, 39.52, 31.24, 28.97, 28.96, 28.92, 28.69, 28.64, 28.54, 25.41, 22.04, 13.89. HRMS (MALDI-TOF): M_n 2349.1, M_w 2382.7, M_z 2415.4.


8.39
8.34
8.33
7.82
7.80
6.98
6.96
4.02
4.01
3.99
3.51
3.24
1.75
1.73
1.71
1.70
1.68
1.25
0.88
0.86
0.84
10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0
f1 (ppm)

(a)


165.68
160.89
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28.97
28.96
28.92
28.69
28.64
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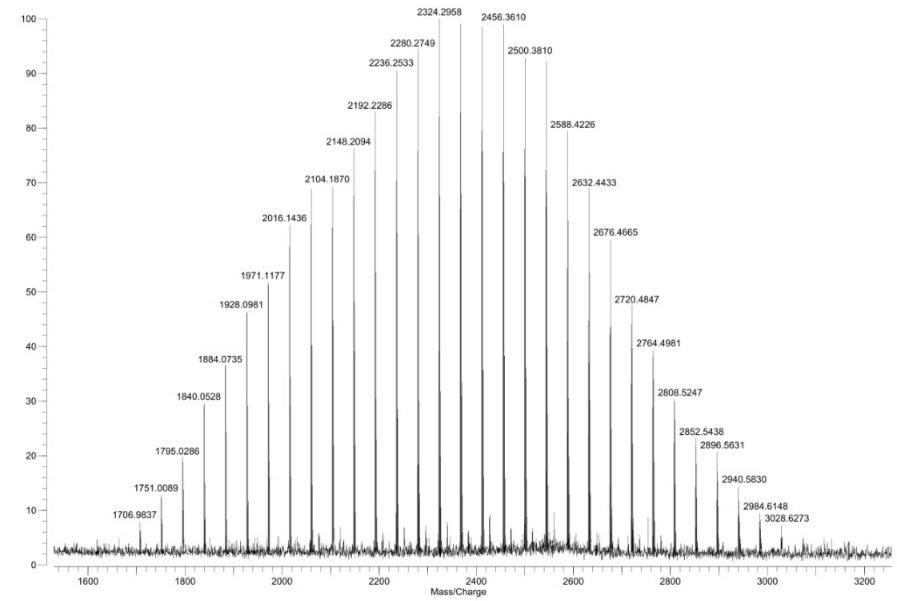
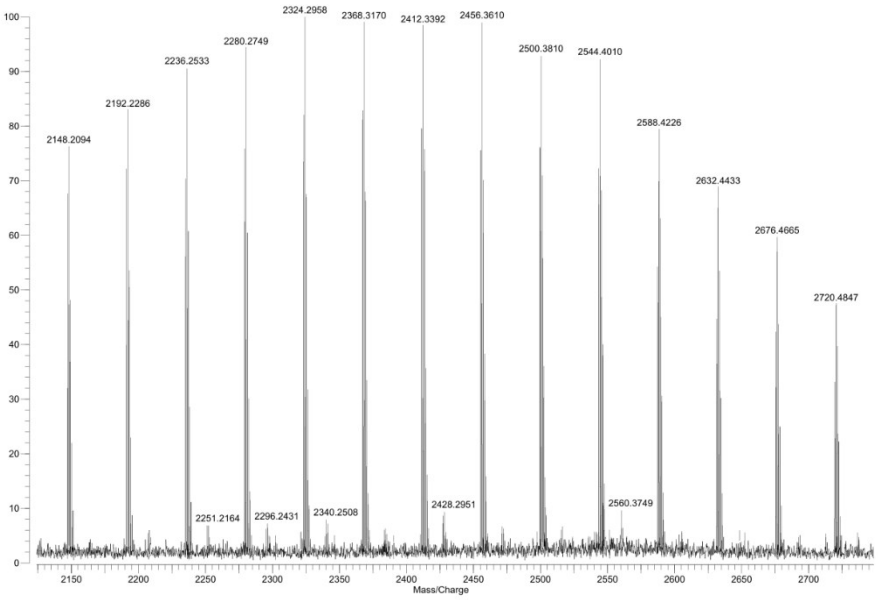
f1 (ppm)

(b)





(c)

Figure S2. (a) ^{1}H NMR spectrum of **PEG-C12** in DMSO-d6; (b) ^{13}C NMR spectrum of **PEG-C12** in DMSO-d6; (c) HRMS (MALDI-TOF) spectrum of **PEG-C12**.

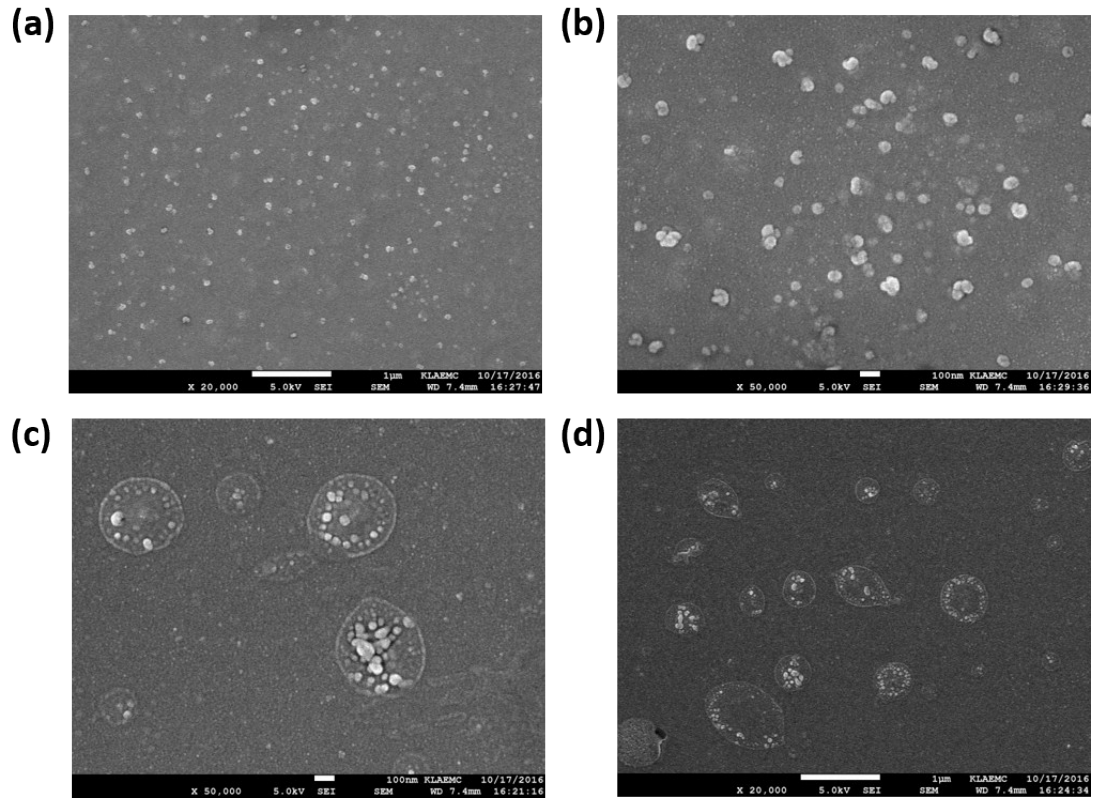


Figure S3. SEM images of the **GC4A** nanoparticles in the absence (a and b) and presence of **TP-TPE** (c and d).

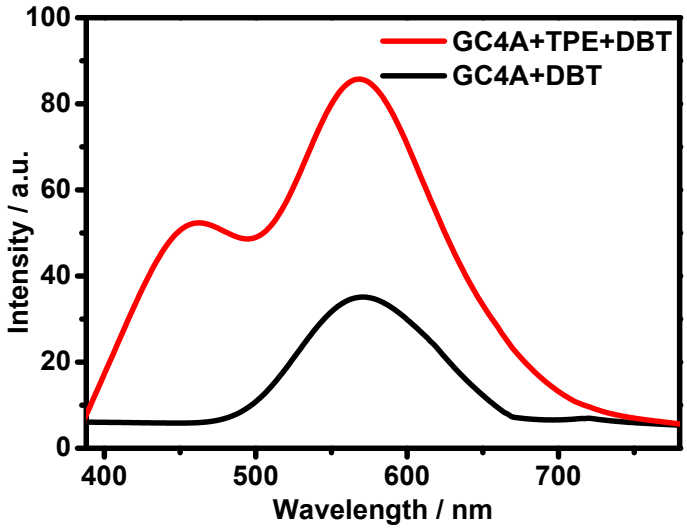
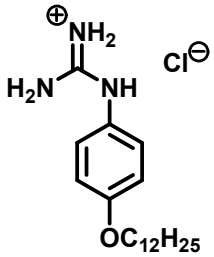


Figure S4. Fluorescence spectra (λ_{ex} = 330 nm) of **DBT** (1 μM) with **GC4A** (50 μM) in the absence and presence of **TP-TPE** (10 μM) in HEPES buffer (10 mM, pH = 6.0)

Förster resonance energy transfer (FRET) based on Gua-12C



Gua-12C

Scheme S3. Chemical structure of **Gua-12C**, the monomer of **GC4A**.

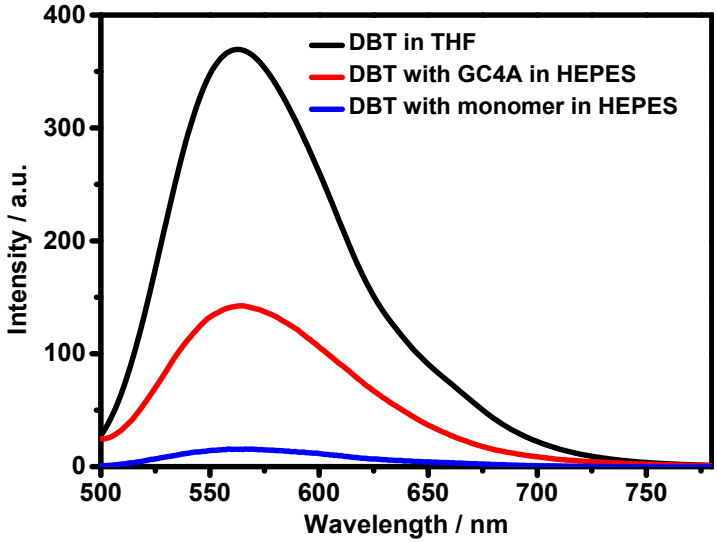


Figure S5. Fluorescence spectra (λ_{ex} = 470 nm) of **DBT** (1 μM) in THF and in the presence of **GC4A** (50 μM) and of **Gua-12C** (200 μM) in HEPES buffer (10 mM, pH = 6.0).

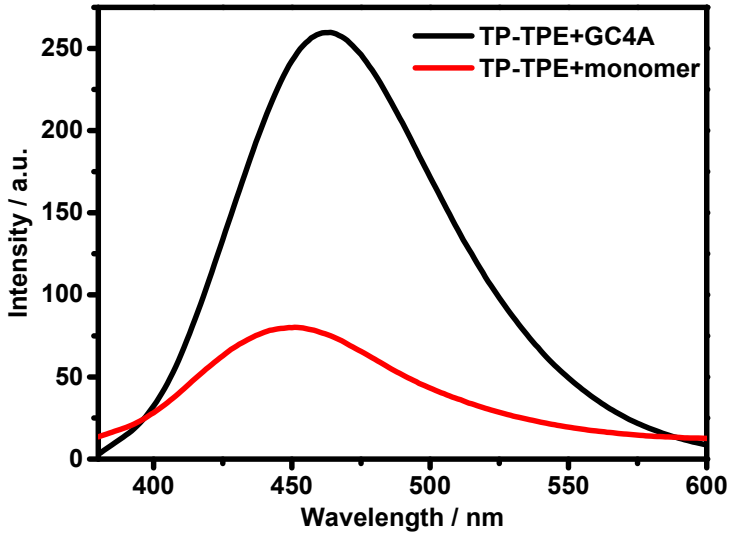


Figure S6. Fluorescence spectra (λ_{ex} = 330 nm) of **TP-TPE** (10 μM) in the presence of **GC4A** (50 μM) and of **Gua-12C** (200 μM) in HEPES buffer (10 mM, pH = 6.0).

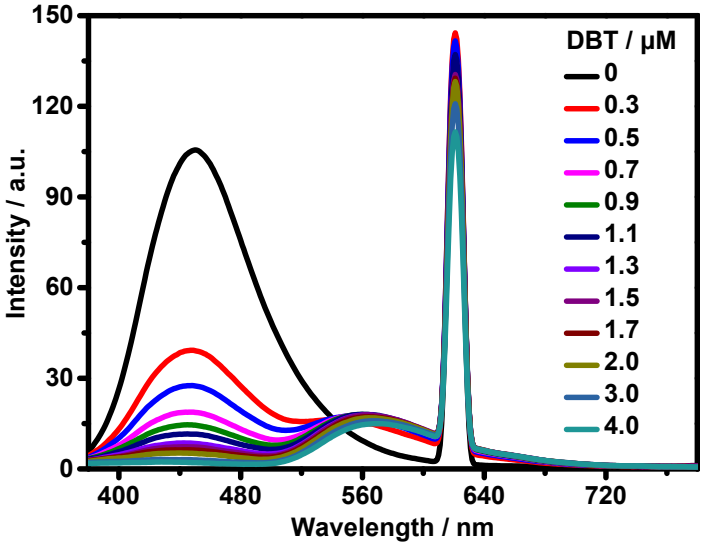


Figure S7. Fluorescence spectra of **TP-TPE@Gua-12C** with different concentrations of **DBT**, λ_{ex} = 310 nm, [**Gua-12C**] = 200 μM, [**TP-TPE**] = 10 μM. The emission peaks at 620 nm are overtone bands.

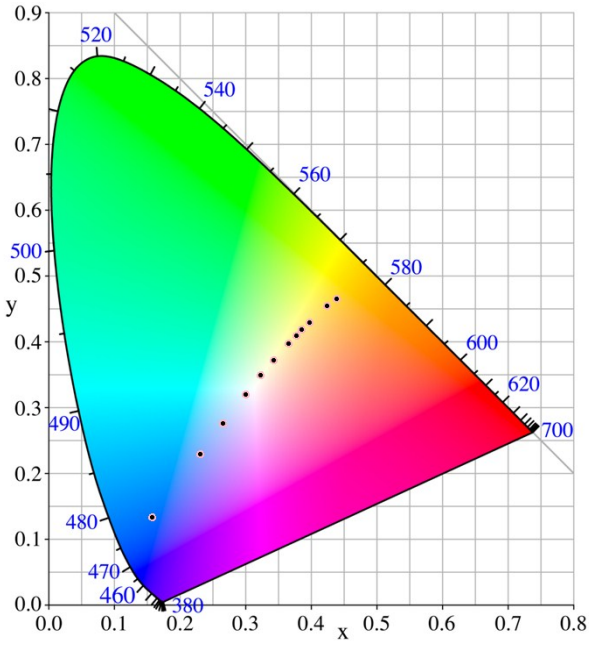


Figure S8. The CIE chromaticity diagram that shows the luminescent color changes of **TP-TPE@ Gua-12C** with different concentrations of **DBT**.

Calculations of FRET efficiency (Φ_{FRET})

FRET efficiency, Φ_{FRET}, the fraction of the absorbed energy that is transferred to the acceptor is experimentally measured as a ratio of the fluorescence intensities of the donor in the absence and presence of the acceptor (I_D and I_{DA}).[4]

$$\Phi_{FRET} = 1 - \frac{I_{DA}}{I_D}$$

Φ_{FRET} was calculated as 70%, measured in the condition of **GC4A/TP-TPE/DBT** = 50/10/1 μM, λ_{em} = 470 nm.

Fluorescence quantum yield measurements

The fluorescence quantum yields were determined using the following formula:[5]

$$\varphi_i = \varphi_S \cdot \frac{n^2}{n_S{}^2} \cdot \frac{I_i}{I_S} \cdot \frac{1-10^{-A_S(\lambda_{exc})}}{1-10^{-A_i(\lambda_{exc})}}$$

where φ is fluorescence quantum yield, A is the absorbance at the excitation wavelength, I the area under the fluorescence spectra, and n is the refractive index of the solvent in which the sample was collected. The subscripts "*i*" and "*S*" refer to the sample of interest and the standard, respectively. Coumarin 153 in EtOH (φ = 0.546)[6] was used as a standard. The quantum yields were thus estimated to be 45.9% for the **TP-TPE/GC4A** assembly, 19.0% for the **TP-TPE/GC4A/DBT** assembly and 0.1% for the free **TP-TPE**, respectively.

Fluorescence lifetime measurements

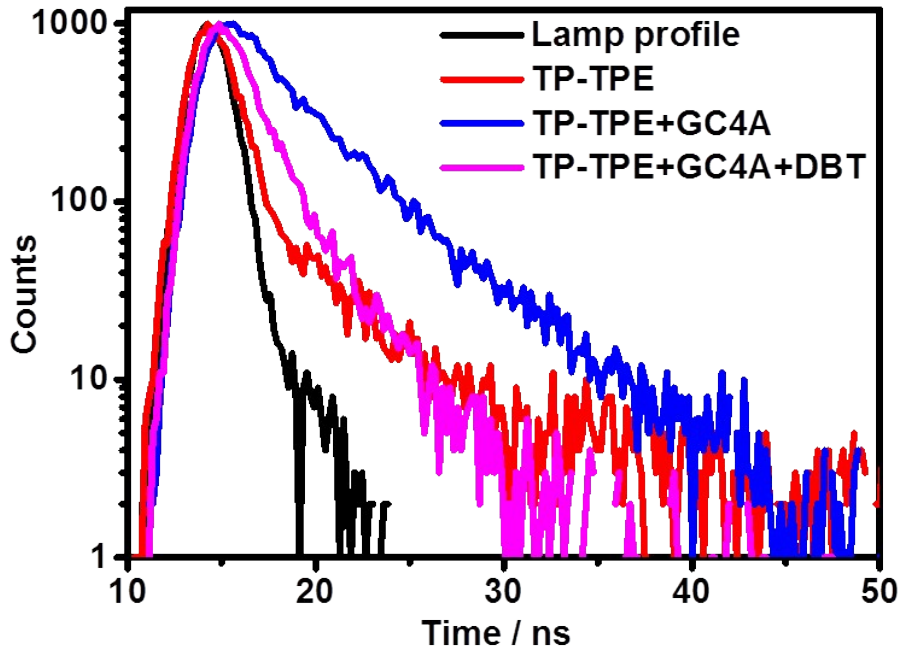


Figure S9. Fluorescence decay profiles of **TP-TPE** (10 μM), **GC4A/TP-TPE** (50/10 μM) and **GC4A/TP-TPE/DBT** (50/10/1 μM) in HEPES buffer (10 mM, pH = 6.0), λ_{ex} = 330 nm.

1. (a) N. Moridi, C. Wackerlin, V. Rullaud, R. Schelldorfer, T. A. Jung and P. Shahgaldian, *Chem. Commun.*, 2013, **49**, 367-369; (b) H. Miel and S. Rault, *Tetrahedron Lett.*, 1997, **38**, 7865-7866.
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3. X. M. Hu, Q. Chen, J. X. Wang, Q. Y. Cheng, C. G. Yan, J. Cao, Y. J. He and B. H. Han, *Chem. - Asian J.*, 2011, **6**, 2376-2381.
4. H. Q. Peng, L. Y. Niu, Y. Z. Chen, L. Z. Wu, C. H. Tung and Q. Z. Yang, *Chem. Rev.*, 2015, **115**, 7502-7542.
5. B. Valeur, *Molecular Fluorescence Principles and Applications*, Wiley-VCH, 2001.
6. K. Rurack and M. Spieles, *Anal. Chem.*, 2011, **83**, 1232-1242.