Novel rare earth fluorescent supramolecular polymeric assemblies constructed by orthogonal pillar[5]arene-based molecular recognition, Eu(III)–coordination and π – π donor–acceptor interactions

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1. Materials and methods

All reagents were commercially available and used as supplied without further purification. ¹H NMR spectra DOSY and NOESY NMR spectrum were recorded with a Bruker Avance DMX 400 spectrophotometer or a Bruker Avance DMX 500 spectrophotometer with use of the deuterated solvent as the lock and the residual solvent or TMS as the internal reference. The samples for NMR measurements were prepared by mixing **EtP5**, **1**, **2** and Eu(NO₃)₃ in molar ratio of 2:2:1:1</sub> in CDCl₃/THF- d_8 ($\nu/\nu = 1/1$) with certain concentrations. Viscosity measurements were carried out with a Cannon-Ubbelohde semi-micro dilution viscometer at 298K in CHCl₃/THF ($\nu/\nu = 1:1$). Scanning electron microscopy (SEM) investigation was carried out on a JEOL 6390LV instrument. The fluorescence spectra were recorded on a Perkin Elmer LS55 fluorescence spectrophotometer. The samples for SEM investigation were prepared by high-concentration solution (100 mM) of (**EtP5**₂•**2**•**1**₂•**E**u)_{*n*}. The solution was dropped onto the silica slices and drawn by needle to form rod-like fibers manually. Then those samples were frozen and vacuum-dried immediately. Before observation, the sample was coated with gold. UV-Vis spectra were taken on a Perkin-Elmer Lambda 35 UV-Vis spectrophotometer.

2. Synthesis of compounds 1 and 2

Compounds $1^{S1,S2}$ and $2^{S3,S4}$ were prepared according to previously reported procedures. The ¹H NMR spectrum of **1** is shown in Fig. S1. ¹H NMR spectrum of **1** (400 MHz, 298 K) in CDCl₃ δ (ppm): 8.73–8.66 (m, 6H), 7.89–7.86 (m, 4H), 7.37–7.36(m, 2H), 7.02 (d, *J* = 8.0 Hz, 2H), 4.03 (t, *J* = 6.0 Hz, 2H), 3.42 (t, *J* = 6.0 Hz, 2H), 1.90–1.79 (m, 4H), 1.51-1.26 (m, 12H).



Figure S1. ¹H NMR spectrum of 1 (400 MHz, 298 K) in CDCl₃.

The ¹H NMR spectrum of **2** is shown in Fig. S2. ¹H NMR spectrum of **2** (400 MHz, 298 K) in CDCl₃ δ (ppm): 8.26 (s, 2H), 3.75 (t, J = 6.0 Hz, 4H), 1.73–1.65 (m, 4H), 1.38 (m, 4H), 0.96 (t, J = 8.0 Hz, 6H).



Figure S2. ¹H NMR spectrum of 2 (400 MHz, 298 K) in CDCl₃.

3. Partial ¹H NMR spectra of **EtP5** and **1** in CDCl₃/THF-d₈ (v/v = 1/1)



Figure S3. Partial ¹H NMR spectra (400 MHz, 298 K) in CDCl₃/THF- d_8 (v/v = 1/1): (a) 5.00 mM **EtP5**; (b) 5.00 mM **EtP5** and 1; (c) 5.00 mM 1.



Figure S4. Partial ¹H NMR spectra (400 MHz, 298 K) in CDCl₃/THF- d_8 (v/v = 1/1): (a) 5.00 mM **EtP5**; (b) 5.00 mM **EtP5** and 1; (c) 5.00 mM 1.



Figure S5. Partial ¹H NMR spectra (400 MHz, 298 K) in CDCl₃/THF- d_8 (v/v = 1/1): (a) 5.00 mM **EtP5**; (b) 5.00 mM **EtP5** and 1; (c) 5.00 mM 1.

4. NOESY NMR spectrum of *EtP5* and 1 in CDCl₃/THF-d₈ (v/v = 1/1)



Figure S6. Partial NOESY NMR spectrum (500 MHz, 298 K) in $CDCl_3/THF-d_8$ (v/v = 1/1) of 10.0 mM **EtP5** and 1.

5. Partial ¹H NMR spectra of $EtP5_2 \cdot 2 \cdot 1_2 \cdot Eu$ complex at different concentrations



Figure S7. Partial ¹H NMR spectra (500 MHz, 298K) of $EtP5_2 \cdot 2 \cdot 1_2 \cdot Eu$ complex in $CDCl_3/THF \cdot d_8$ ($\nu/\nu = 1/1$) at different concentrations: (a) 5.00 mM; (b) 10.0 mM; (c) 15.0 mM; (d) 20.0 mM; (e) 25.0 mM; (f) 50.0 mM; (g) 75.0 mM; (h) 100 mM.



Figure S8. Partial ¹H NMR spectra (500 MHz, 298K) of $EtP5_2 \cdot 2 \cdot 1_2 \cdot Eu$ complex in $CDCl_3/THF \cdot d_8$ (v/v = 1/1) at different concentrations: (a) 5.00 mM; (b) 10.0 mM; (c) 15.0 mM; (d) 20.0 mM; (e) 25.0 mM; (f) 50.0 mM; (g) 75.0 mM; (h) 100 mM.



Figure S9. Partial ¹H NMR spectra (500 MHz, 298K) of $EtP5_2 \cdot 2 \cdot 1_2 \cdot Eu$ complex in CDCl₃/THF-*d*₈ (*v*/*v* = 1/1) at different concentrations: (a) 5.00 mM; (b) 10.0 mM; (c) 15.0 mM; (d) 20.0 mM; (e) 25.0 mM; (f) 50.0 mM; (g) 75.0 mM; (h) 100 mM.

6. DLS results of EtP5₂•2•1₂•Eu complex at low concentration and high concentration



Figure S10. DLS results of EtP5₂•2•1₂•Eu complex at different concentrations: (a) 5.00 mM; (b) 200 mM.

7. Scanning electron micrograph of rod-like fibers



Figure S11. Scanning electron micrograph of a rod-like fiber drawn from a high-concentration solution (100 mM) of $(EtP5_2 \cdot 2 \cdot 1_2 \cdot Eu)_n$.

8. Photostability of $(EtP5_2 \cdot 2 \cdot 1_2 \cdot Eu)_n$ polymer under day light



Figure S12. Fluorescent changes of the supramalecular polymer $(EtP5_2 \cdot 2 \cdot 1_2 \cdot Eu)_n$ in 46 hours. The sample was kept under day light.

The fluorescent changes of the polymer $(EtP5_2 \cdot 2 \cdot 1_2 \cdot Eu)_n$ (100 mM) during 2 days (46 h) was tested to check the property of photostability when exposing to the day light. The fluorescent spectrum was measured every 1 hour and after 10 hours later measured every 12 hours. During this time, the sample

was kept under day light. The resulted spectra showed slightly changes in 46 hours indicating relatively good photostability.

9. Calculation of the degree of polymerization

According to the Stokes-Einstein relationship^{S5} and the diffusion coefficient, the average degree of polymerization was estimated by the data from DOSY.^{S6} Supposing that **EtP5**₂•2 complex and **1**₂•Eu complex were A_2 type and B_2 type monomer of the polymer respectively, the average weight *M* of the polymer at 100 mM was 618.0 kg/mol, which corresponds to an average degree of polymerization of 34 calculated from the following calculation

$$\log D = -\frac{1}{3}\log M + \frac{1}{3}\log \rho - \log \eta - \frac{1}{3}\log \frac{162\pi^2}{k^3 T^3 N_A}$$
(1)

where k is the Boltzmann constant, T is the absolute temperature, η is the solvent viscosity, ρ is the density of the liquid and N_A is the Avogadro constant. The diffusion coefficient D of monomers $1/2(\text{EtP5}_2 \cdot 2 \cdot 1_2 \cdot \text{Eu})$ at 100 mM is $2.01 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$, the absolute temperature T is 298 K, the solvent viscosity η is $5.60 \times 10^{-4} \text{ Pa} \cdot \text{s}$ and the density of the liquid ρ is $1.19 \times 10^3 \text{ kg/m}^3$.

10. References:

- S1. K. Jie, Y. Zhou, B. Shi and Y. Yao, Chem. Commun., 2015, 51, 8461.
- S2. L. Wu, C. Han, X. Wu, L. Wang, Y. Caochen and X. Jing, Dalton Trans., 2015, 44, 20334.
- S3. S. De and S. Ramakrishnan, *Macromolecules.*, 2009, 42, 8599.
- S4. S. Wang, Y. Wang, Z. Chen, Y. Lin, L. Weng, K. Han, J. Li, X. Jia and C. Li, *Chem. Commun.*, 2015, 51, 3434.
- S5. W. Li, H. Chung, C. Daeffler, J. A. Johnson, R. H. Grubbs, Macromolecules., 2012, 45, 9595.
- S6. H. Wang, P. Wang, H. Xing, N. Li and X. Ji, J. Polym. Sci., Part A: Polym. Chem., 2015, 53, 2079.