# **Electronic Supplementary Information (ESI)**

# Tailoring luminescent color conversion *via* affinitive coassembly of glutamates appended with pyrene and naphthalene dicarboximide units

Pengyao Xing<sup>a,b</sup>, Zhuo Zhao<sup>c</sup>, Aiyou Hao\*<sup>b</sup> and Yanli Zhao\*<sup>a,d</sup>

<sup>a</sup>Division of Chemistry and Biological Chemistry, School of Physical and Mathematical Sciences, Nanyang Technological University, 21 Nanyang Link, Singapore 637371, Singapore. E-mail: zhaoyanli@ntu.edu.sg

<sup>b</sup>School of Chemistry and Chemical Engineering and Key Laboratory of Colloid and Interface Chemistry of Ministry of Education, Shandong University, Jinan 250100, PR China. E-mail: haoay@sdu.edu.cn

<sup>c</sup>Technical Center for Safety of Industrial Products, Tianjin Entry–Exit Inspection Quarantine Bureau, No. 2 Dong Wu Road, Tianjin 300308, PR China

<sup>d</sup>School of Materials Science and Engineering, Nanyang Technological University, Singapore 639798, Singapore

# **Experimental section**

# Materials

All chemicals were purchased from Sigma-Aldrich and used without further purifications. NG and PG were synthesized according to our previous report.<sup>S1</sup>

# Characterizations

<sup>1</sup>H NMR spectra were measured on a Bruker-AC 300 spectrometer. Absorption spectra were recorded on a Shimadzu UV-3600 spectrophotometer. Fluorescence emission spectra were recorded on a Shimadzu RF-

5301pc fluorescence spectrophotometer. Fluorescence decay profiles were measured on an ISS K2 system with a phase modulation model using a scattering sample as standard. TEM images were collected on a JEM-1400 (JEOL). DLS size distributions were measured on a Nanobrook 90Plus particle size analyzer.

#### Methods

For the preparation of vesicles, concentrated solutions (10 mM) of PG and NG in deionized water (DI water) were first prepared. Then, a certain amount of concentrated solutions was transferred into small vials by pipette, followed by dilution. After that, the diluted solution was subjected to sonication for 15 minutes, and then stabilized for several hours before characterization. The preparation of mixed vesicle systems also followed the similar procedure. A certain amount of concentrated PG and NG solutions was added together. The mixture solution was gently shaken to make homogeneous, and then it was diluted to give desired co-assembled vesicles.



Figure S1 TEM images of PG and NG vesicles at different concentration ranges.



Figure S2 Concentration-dependent DLS size distributions of PG upon increasing the concentration.



Figure S3 Concentration-dependent DLS size distributions of NG upon increasing the concentration.



Figure S4 TEM images of co-assembled vesicles. (a)  $C_{PG}$ : 5 mM, NG: 5 mol%; (c-d)  $C_{PG}$ : 5 mM, NG: 10 mol%.



Figure S5 Negatively stained TEM image of PG/NG co-assemblies (C<sub>PG</sub>: 5 mM, NG: 5 mol%).

### Discussions regarding the co-assembly process of PG and NG

The concentrated PG and NG mother solutions were first prepared, and they were mixed with appropriate molar ratios followed by dilution to give the co-assembled vesicle system. In this process, the mixed vesicles would undergo sonication that can provide extra energy to accelerate the interdigitation of NG and PG. Actually, direct addition of NG into PG vesicles could also form the co-assembled vesicles, though higher energy may be needed. As we know, the vesicles have dynamic and flexible membranes constituted by amphiphiles. They are metastable in aqueous media. When induced by some stimuli, membrane movement events like membrane fusion, disassociation, and fission may occur. Unlike other stable aggregates such as nanofibers and nanoparticles, vesicle membranes are capable of changing shapes because of dynamic amphiphile movement. These dynamic processes contain amphiphile exchange, lateral diffusion as well as flip-flop. It means that, the vesicle membranes could exchange amphiphiles with the monomers in ambient environment. In our case, once NG molecule was added into the PG vesicle system, due to their high affinity and binding constant, NG could insert into the packed PG layer in vesicle membranes spontaneously through the membrane movement. Even without external energy like sonication, after a moderate period, co-assembled vesicles could also be formed.



**Figure S6** FT-IR spectra of freeze-dried samples of PG (5 mM), NG (5 mM) as well as PG/NG complex (5 mM).



**Figure S7** (a) Aromatic proton shifts of PG and NG upon increasing the NG molar fractions in Fig. 1c. (b) Determination of binding constant between NG and PG *via* Benesi–Hildebrand equation and <sup>1</sup>H NMR titrations.



**Figure S8** (a) <sup>1</sup>H NMR spectra of co-assembled PG/NG system with different molar ratios of NG:PG; (b) Job's plot curve calculated from (a).



**Figure S9** Concentration-dependent absorption spectra of NG upon increasing the concentration from 0.01 mM to 0.5 mM.



**Figure S10** Concentration-dependent absorption spectra of PG upon increasing the concentration from 0.01 mM to 0.2 mM.



**Figure S11** Absorption spectral comparison between aggregation and monomer solutions of PG and NG. Slight blue shift of PG and red shift of NG after aggregation indicate the presence of H-type and J-type  $\pi$ - $\pi$  stacking in PG and NG vesicles, respectively.



Figure S12 Concentration-dependent emission spectra of NG upon increasing the concentration.



**Figure S13** Concentration-dependent emission spectra of PG upon increasing the concentration from 0.1 mM to 10 mM.



**Figure S14** Digital images of (a) monomer and (b) excimer emission colors of PG and (c) excimer emission color of NG in aqueous media.



**Figure S15** Overlapped areas between the emission of PG and the absorption of NG at (a) low and (b) high concentration conditions of PG.



**Figure S16** (a) Emission spectra of PG/NG mixtures upon increasing the NG molar fractions ( $C_{PG}$ = 1 mM). (b) Optical images of co-assembled samples with different molar fraction of NG. (c) Emission colors of co-assembled samples ( $C_{PG}$  = 1 mM).



Figure S17 Emission spectra of PG/NG mixtures upon increasing the NG molar fractions (C<sub>PG</sub>= 2 mM).



Figure S18 Emission spectra of PG/NG mixtures upon increasing the NG molar fractions ( $C_{PG}$ = 5 mM).



Figure S19 Energy transfer efficiency profile upon increasing the NG molar fractions.



Figure S20 Emission spectra of NG with and without the presence of PG at the same concentration.



**Figure S21** Life time decay profiles of PG with different NG in co-assembled system ( $\lambda_{em}$  = 480 nm).



Figure S22 Temperature-dependent emission spectra of PG in water (5 mM).



Figure S23 Temperature-dependent emission spectra of NG in water (5 mM).



Figure S24 Temperature-dependent emission spectra of PG/NG mixture in water (C<sub>PG</sub> = 2 mM, 3 mol% NG).



**Figure S25** Temperature-dependent emission spectra of PG/NG mixture in water ( $C_{PG}$  = 5 mM, 10 mol% NG).

### **Discussion regarding temperature-dependent emission**

Figures S22-S25 display the temperature-dependent fluorescence studies. With the increase in ambient temperature, PG assembly showed a fluorescent quenching with almost no shift. However, it presented a contrary fluorescent enhancement for NG system. Normally, two fluorescent effects exist in supramolecular aggregation, namely aggregation-caused-quenching (ACQ) and aggregation-induced-emission (AIE). Through concentration-dependent emission studies of NG and PG, it was found that both of these chromospheres belong to ACQ luminophore due to their inevitable quenching upon increasing the concentration. In most cases, supramolecular self-assembly owns thermal-responsive property, because the aggregates would de-assemble at high temperature. Lots of self-assembled structures exhibit this characteristic, such as some vesicle systems and most of physical gels. In our system, however, high temperature (up to 80 °C) would not only quench the emission of excimer emission at 480 nm, but also quench the monomer emission at 396 nm in the case of PG. This means that the PG vesicle is ultra-stable at a high temperature without dissociation because the disassembly would enhance the fluorescence. The

fluorescence quenching is due to the enhanced thermal motion at high temperature, which promotes the thermal irradiation rather than emission. However, the enhancement emission of NG vesicle is due to the disassembly of vesicles, surpassing the loss of thermal irradiation. When we studied the thermal properties of NG-doped PG vesicle (donor-acceptor array), we found that, when increasing the temperature, the emission of donor showed the decreasing tendency. Nevertheless, fluorescent intensity of the acceptor displayed decreasing tendency as well, which is in sharp contrast with the observation for pure acceptor, implying a fact that some input excitation energy is originated from the PG emission (fluorescent resonance energy transfer, FRET).

## Reference

S1. P. Xing, L. Bai, H. Chen, P. H. Tham, A. Hao and Y. Zhao, ChemNanoMat, 2015, 1, 517–527.