

## Supporting Information

### Molecular Recognition Directed Supramolecular Control over Perylene-bisimide Aggregation Resulting in Aggregation Induced Enhanced Emission (AIEE) and Induced Chiral Amplification

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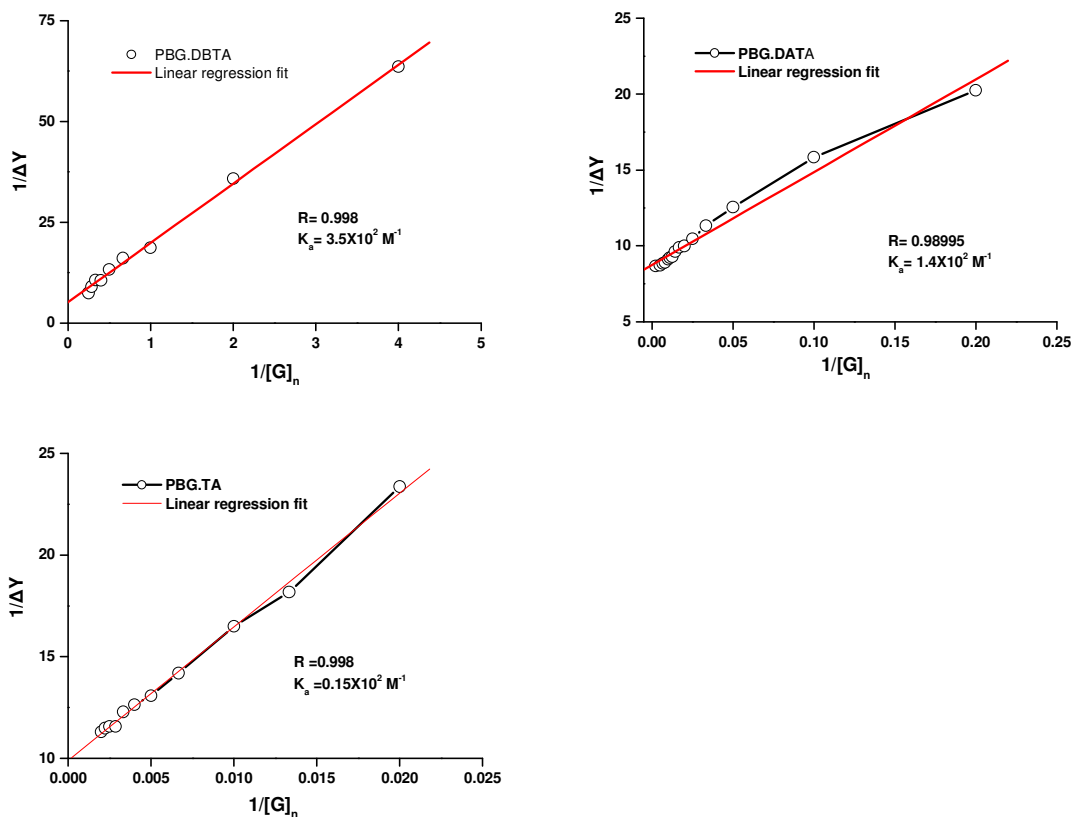
FaX: (+81)92-805-3814

1. Association constant ( $K_a$ ) determination:

Binding constants were calculated according to the Benesi-Hildebrand equation (SI eqn. 1) for the host-guest (H-G) system.  $K_a$  values were calculated following the equation stated below.

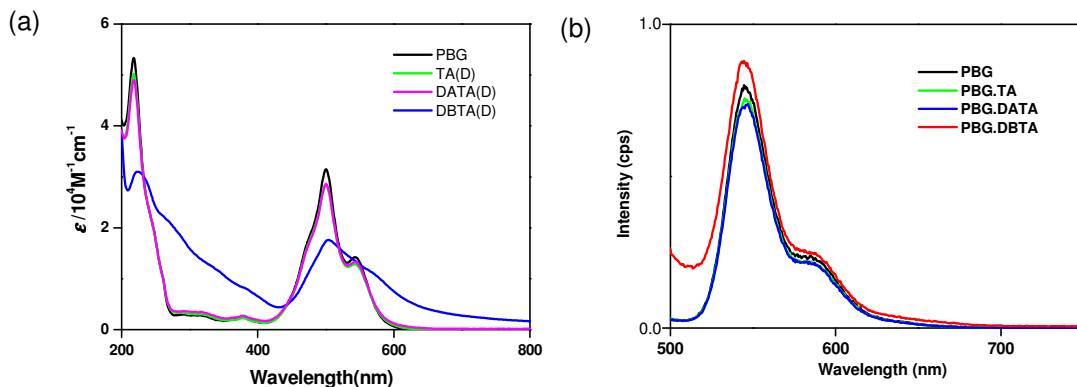
$$\frac{1}{\Delta Y} = \frac{1}{Y_{\Delta HG} K_a [G]_n} + \frac{1}{Y_{\Delta HG}} \quad \dots\dots\dots \text{(SI eqn. 1)}$$

The mathematical model was used to obtain  $K_a$ , is usually developed from realizing the physical change ( $\Delta Y$ ) (the change in absorbance value) in the presence of added guest,  $[G]_n$ . It was assumed that the observed change is correlated to the concentration of the complex  $[HG]$  as  $\Delta Y \propto [HG]$ . In practice, the two unknown factors in SI eqn. 1 *i.e.*  $K_a$  and  $Y_{\Delta HG}$  were obtained by plotting  $1/\Delta Y$  vs.  $1/[G]_n$  and applying linear regression method.



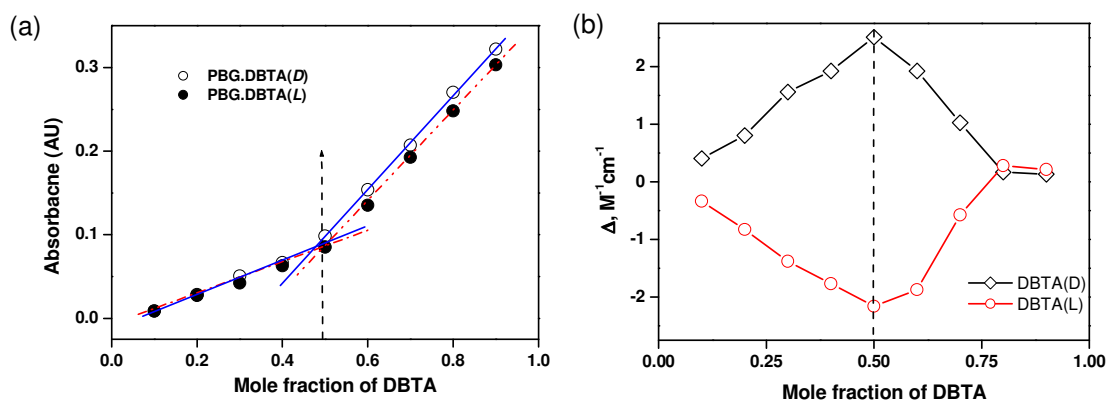
**SI Fig. 1.** The Benesi–Hildebrand plots were obtained by plotting the absorbance data collected from the UV-vis titration of the Host, PBG ( $1.0 \times 10^{-4} \text{ M}$ ) against the guest concentrations ( $[G]_n$ ), measured at constant  $\lambda_{\text{ex.}} = 500 \text{ nm}$ .

## 2. Aggregate formation of PBG with TA derivatives:



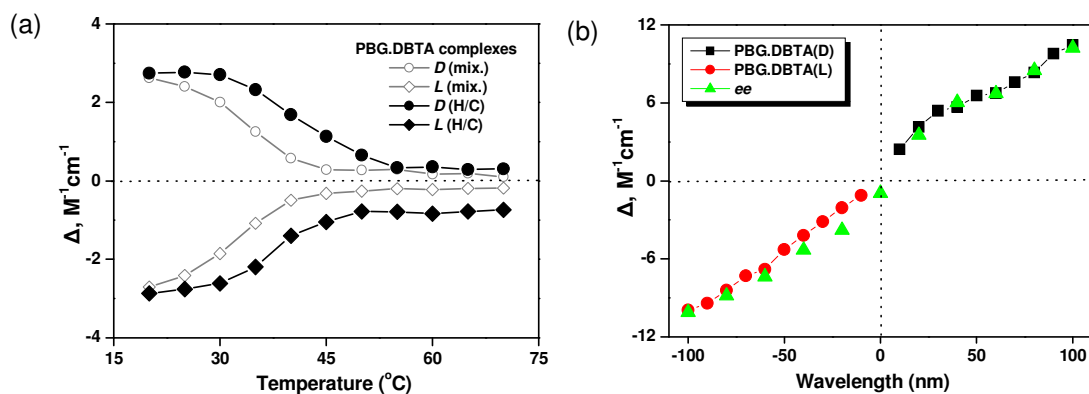
**SI Fig. 2.** (a) Absorbance spectra and (b) Fluorescence spectra of PBG, and the 1:1 complexes of PBG with different dicarboxylic acids synthesized in H/C method at  $5.0 \times 10^{-5}$  M concentration in pH 7.4 HEPES solution at 20 °C.

## 3. Job's Plot Measurement:



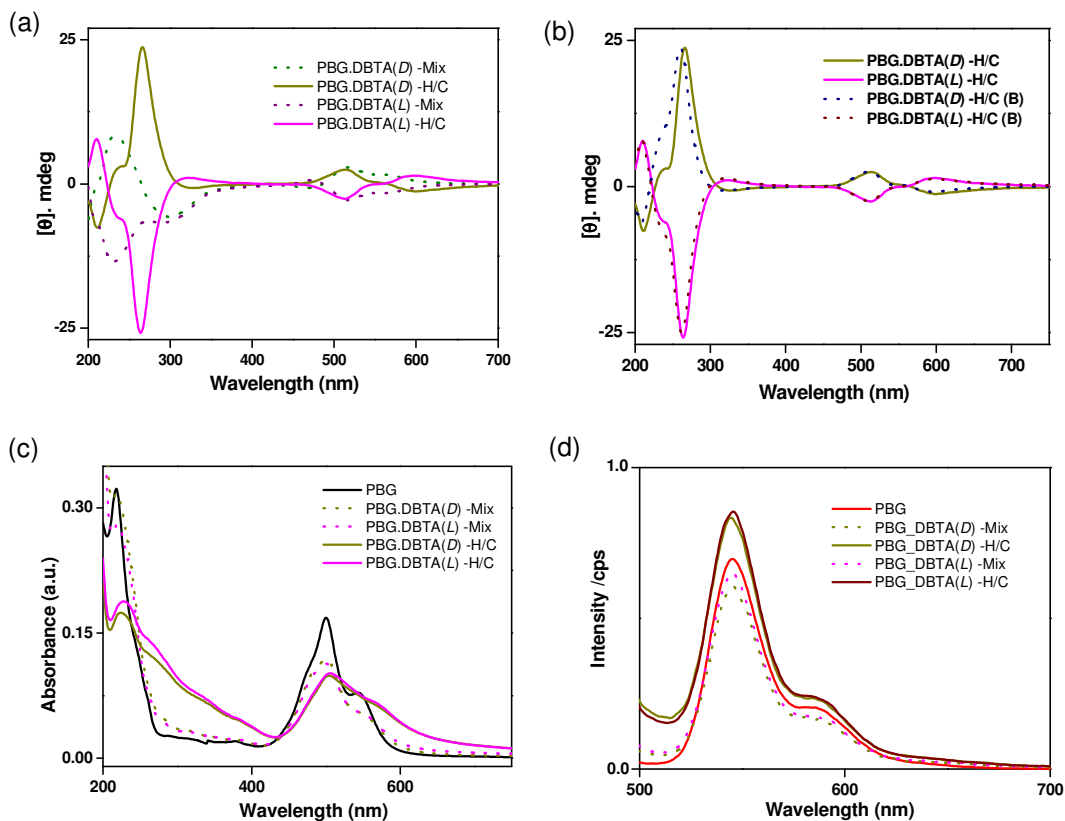
**SI Fig. 3.** Optimum molar ratio for the complex formation was determined by monitoring (a) the absorbance change at  $\lambda_{\text{ex}} = 500$  nm, and (b) the ICD spectra intensity change at 523 nm at total concentration of  $5.0 \times 10^{-5}$  M in pH 7.4 HEPES buffer solution (complexes were prepared in heating-cooling method).

#### 4. ICD measurement at different conditions:



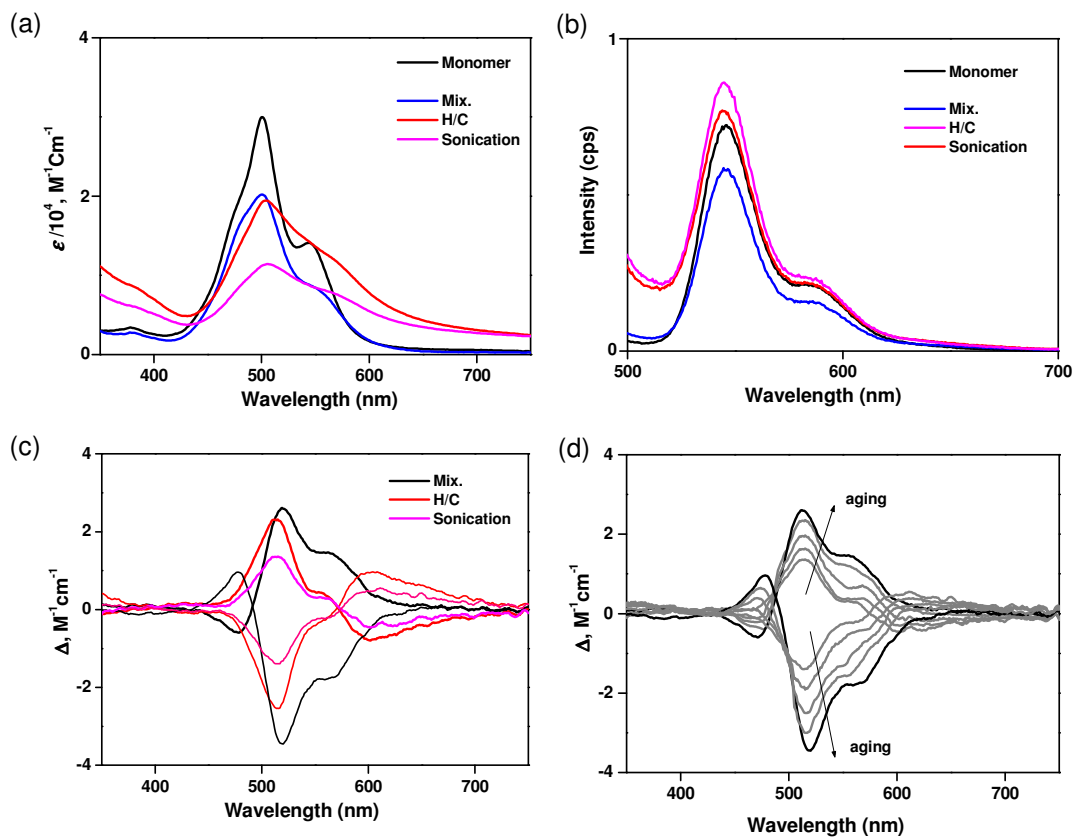
**SI Fig. 4.** (a) The change in ICD intensity at 523 nm with the temperature was plotted for the complexes prepared in different methods in HEPES buffer solution. (b) ICD intensity change against the concentration of different enantiomers and the intensity change in the ee prepared in advance before the addition into the PBG solution in water/methanol = 40:60 v/v solvent in pH 7.4 at 20  $^{\circ}C$ .

5. PBG·DBTA 1:1 complex formation in different conditions:



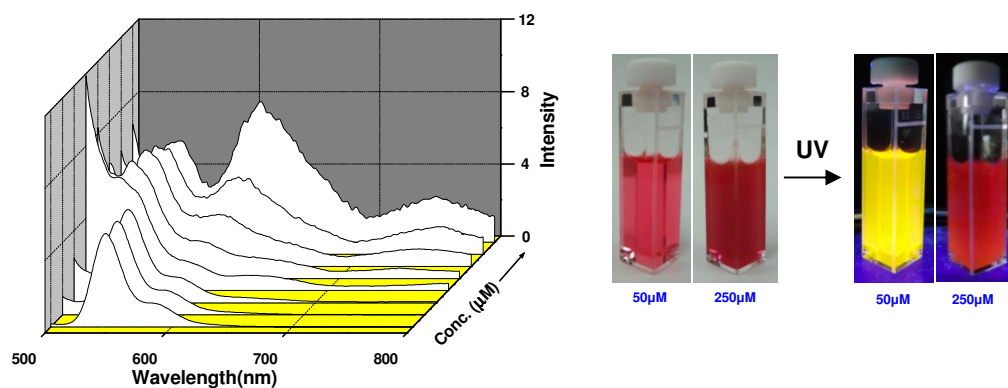
**SI Fig. 5.** Self-assembled complexes of PBG & DBTA (*D/L*) ( $5.0 \times 10^{-5}$  M) were prepared by simple mixing (Mix) and heating-cooling method (H/C) at 1:1 mole ratio and in pH 7.4 HEPES buffer solution: (a) Induced CD spectra of the 1:1 complexes in water (W), (b) in Buffer(B), (c) UV-vis spectra of only PBG and the complexes formed in different conditions, and (d) corresponding fluorescence spectra in HEPES buffer solution at 20 °C.

6. Complex properties depend on external stimuli:



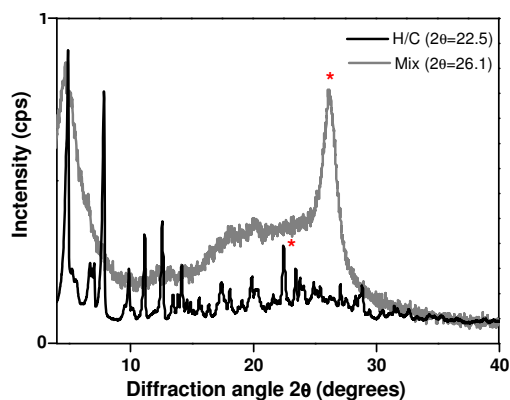
**SI Fig. 6.** (a-c) The spectroscopic measurement data of the PBG monomer and PBG·DBTA ( $D/L$ ) complexes ( $5.0 \times 10^{-5} M$ ) prepared in different conditions and in presence of shear as stimuli, and (d) Recovery of the ICD spectral intensity over a time (about 1 hr.) after applying sonication for 5 minutes on the PBG·DBTA ( $D/L$ ) complexes prepared in H/C method in pH 7.4 HEPES buffer solution.

## 7. Concentration effect in fluorescence emission:



**SI Fig. 7.** (left) Fluorescence change was studied in the concentration range between  $1.25 \times 10^{-5}$  to  $5.0 \times 10^{-4}$  M (normalized against the *FL* intensity at 545 nm), (right) visual color change of the 1:1 complex solutions at different concentrations under normal light and UV lamp (at 365 nm).

## 8. Wide-angle X-ray scattering:

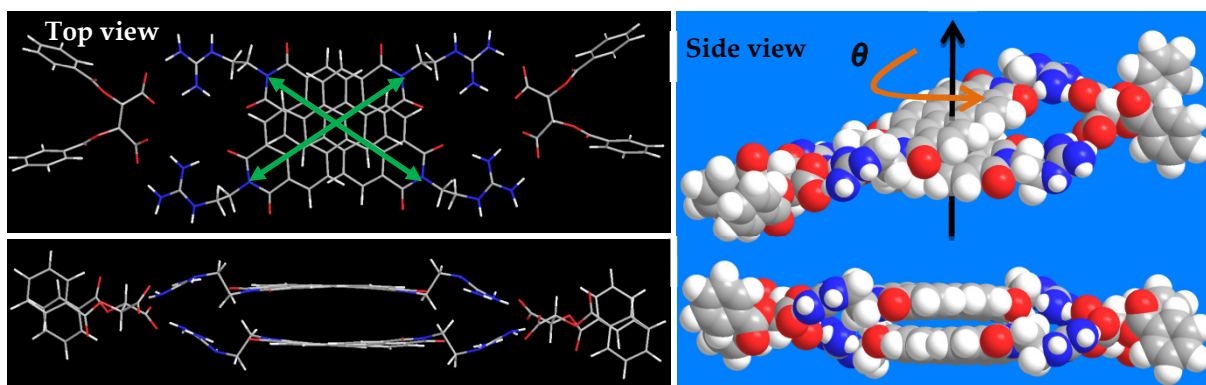


**SI Fig. 8.** Wide-angle X-ray scattering of the fridge-dried self-assembled PBG-DBTA complexes prepared in Mix and in H/C methods (calculated  $\pi$ -stacking distances are 3.9 and 3.4 Å, respectively).

## 9. Molecular Modeling.

All the structures were calculated by considering 2+2 box-type dimeric structure formation at the molar ratio of 1:1, we calculated the possible dimeric structure using trial and error. The complex between PDI and DBTA are calculated by MOPAC with PM6-DH2 Hamiltonian and COSMO (conductor like Screening Model for Realistic Solvation) method; using dielectric constant value of water, 78.4 eps.

The PBG-DBTA complex structure with lowest heat of formation shows positive chiral biasness along the growth axis. The structure exhibits stable hydrogen bonding between guanidine group of PBG and carboxylate group of the DBTA. The benzoyl (Bz) groups of DBTA occupy the outer space, and the perylene  $\pi$ -cores show non-coplanar distorted stacking nature along the growth axis. From the closed packing structure (below) one can easily predict the generation of chirality in the stacked pattern, and the angle between the dipoles was measured by drawing lines (as shown below, green) on the top view image.



Heat of Formation = -828.5 Kcal  
Dipole moment = 3.7 D  
 $\pi$ -stacking distance is 3.7 Å

SI reference: (1) H.A. Benesi and J. H. Hildebrand, *J. Am. Chem. Soc.*, 1949, **71**, 2007.