Electronic Supplementary Information

Helical Supramolecular Aggregates of Sugar-based Perylene Devs: Effect of Core-substituted Groups

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1. Synthesis and characterization of PTCDI-BAG and PTCDI-ClBAG.

N,*N*'-bis((4-aminophenyl)- β -D-glucopyranoside)-perylene-3,4:9,10-tetracarboxylbisimide (PTCDI-HAG). 3, 4 : 9, 10-perylenetetracarboxylbisimide (0.094 g, 0.2 mmol) and (4-Aminophenyl)- β -D-glucopyranoside (0.13 g, 0.48 mmol), Zn(OAc)₂ (0.20 g) in imidazole (6 g) and stirred for 2 h at 120 °C under N₂. The reaction mixture was cooled to room temperature and H₂O (5 mL) and C₂H₅OH (30 mL) added to the mixture. The dark red precipitate was filtered, washed with distilled water, and dried in vacuum at 60 °C. This solid was further purified by recrystallization with DMF/C₂H₅OH to give the dark red solid (0.15 g, 80%).¹H NMR (400 MHz, DMSO-*d*₆): 3.32 (m, 2H), 4.16 (m, 4H), 4.29(m, 4H), 4.71 (m, 2H), 5.23 (m, 2H), 5.32 (d, 4H, *J* = 5.5 Hz), 5.43 (s, 2H), 5.64 (s, 2H),7.47-7.72 (m, 8H), 8.47 (d, 8H, J = 26.6 Hz). MS (MALDI-TOF): calcd for C₄₈H₃₈N₂O₁₆, 898.2 m/z, found 898.2. Anal. Calcd for C₄₈H₃₈N₂O₁₆ : C, 64.14; H, 4.26; N, 3.12. Found: C,63.65; H, 4.12; N, 3.43.

N,N'-bis((4-aminophenyl)-α-D-glucopyranoside)-perylene-3,4:9,10-

tetracarboxylbisimide (PTCDI-ClBAG). 1,6,7,12-tetrachloroperylene-3,4,9,10tetracarboxylic acid bisanhydride (0.10 g, 0.19 mmol), and (4-Aminophenyl)- β -Dglucopyranoside (0.13 g, 0.48 mmol), Zn(OAc)₂ (0.20 g) in imidazole (6 g) and stirred for 2 h at 120 °C under N₂. The reaction mixture was cooled to room temperature and H₂O (5 mL) and C₂H₅OH (30 mL) added to the mixture. The dark red precipitate was filtered, washed with distilled water, and dried in vacuum at 60 °C. This solid was further purified by recrystallization with DMF/C₂H₅OH/n-C₆H₁₄ to give the dark red solid (0.14 g, 72%).¹H NMR (400 MHz, CD₃COOF- d_6): 3.36 (m, 2H), 4.12 (m, 4H), 4.33 (m, 4H), 4.76 (m, 2H), 5.18 (m, 2H), 5.32 (d, 4H, J = 5.6 Hz), 5.41 (s, 2H), 5.62 (s, 2H),7.45-7.78 (m, 8H), 8.32 (s, 4H). MS (MALDI-TOF): calcd for C₄₈H₃₄Cl₄N₂O₁₆, 1034.1 m/z, found 1034.2. Anal. Calcd for C₄₈H₃₄Cl₄N₂O₁₆ : C, 55.62; H, 3.31; N,2.72. Found: C, 55.48; H, 3.12; N, 2.58.

2. Experimental Section

General: To obtain the supramolecular structures, an appropriate amount of PTCDI-BAG and PTCDI-ClBAG was firstly dissolved in 2 mL DMF to obtain a stock solution at a concentration of 1 mg·mL⁻¹, and was then diluted to the required concentration. Water was then injected into DMF solutions of PTCDI-BAG and PTCDI-ClBAG with DMF/H₂O volume ratios of, respectively, with the final PTCDI-BAG and PTCDI-ClBAG concentrations were kept as a constant of 0.05 or 0.08 mg·mL⁻¹. After vigorous stirring for 10 minutes, the samples were kept stationary to self-assemble for different time intervals at room temperature. Circular dichroism (CD) measurements were conducted on a JASCOJ-810 spectrometer at room temperature. UV-vis adsorption spectra were recorded on Perkin-Elmer Lamda 950 UV-vis spectroscopy. ¹H NMR was acquired using a Bruker 400 MHz NMR spectrometer.

Computational methods: The ground-state geometry of the monomers and dimers were optimized using density functional theory (DFT) with the B3LYP functional for monomers and B3LYP functional with Grimme's dispersion (B3LYP-D)¹ for dimers and the 6-31G (d,p) basis set. Based on the optimized structures, time-dependent density functional theory (TDDFT) with the long-range corrected (LRC) functional ω B97x and 6-31G (d,p) basis set was employed to calculate the excitation energies and the electric transition dipole moments and the magnetic transition dipole moments. The ω values for the LRC functional were optimized according to the method reported by Stein el al.² the optimized ω values were equal to 0.15 bohr⁻¹ and 0.14 bohr⁻¹ for PTCDI-BAG and PTCDI-CIBAG dimers, respectively. All the calculations were performed in the gas phase with Gaussian 09 program.³ The CD rotational strength can be evaluated by dipole length-velocity formalism:

$$R_{0i}^{r} = \frac{1}{2c} \left\langle \Psi_{0} \middle| \hat{\mathbf{r}} \times \hat{\nabla} \middle| \Psi_{i} \right\rangle \cdot \left\langle \Psi_{i} \middle| \hat{\mathbf{r}} \middle| \Psi_{0} \right\rangle \quad (1)$$

Where *c* is the speed of light, and *i* is an excited state. It has been shown that the length form R^r yields very reasonable results.⁴ The simulated spectra are obtained as Gaussian convolutions in the following form for absorption and CD spectra, respectively:

$$UV(E) = A \frac{1}{\sqrt{2\pi\sigma}} \sum_{m} \Delta E_{0m} I_{0m} exp - \left[\frac{E - \Delta E_{0m}}{2\sigma}\right]^{2} (2)$$
$$CD(E) = \frac{1}{2.297 \times 10^{-39}} \frac{1}{\sqrt{2\pi\sigma}} \sum_{m} \Delta E_{0m} R_{0m} exp - \left[\frac{E - \Delta E_{0m}}{2\sigma}\right]^{2} (3)$$

 σ is a broading factor, which is set to be 0.1 eV. ΔE_{0m} , I_{0m} and R_{0m} are the excitation energy, the oscillator strength, and the rotational strength for the transition from the ground state $|0\rangle$ to the

excited state $\left|m\right\rangle$. A is the absorption coefficient.

3. Additional figures





Fig. S1 (a) CD and (b) UV-vis spectra of PTCDI-BAG and PTCDI-ClBAG in DMF (0.05 mg.mL⁻¹).



Fig.S2 CD spectra of PTCDI-ClBAG in 80/20 DMF/H₂O (0.05 mg.mL⁻¹).



Fig. S3 CD spectra of PTCDI-BAG in DMF/C₂H₅OH (0.05 mg.mL⁻¹).



Fig. S4 CD spectra of PTCDI-ClBAG in DMF/C₂H₅OH (0.05 mg.mL⁻¹).



Fig. S5 CD spectra of PTCDI-BAG in DMF/H₂O (0.08 mg.mL⁻¹).



Fig. S6 CD spectra of PTCDI-ClBAG in DMF/H₂O (0.08 mg.mL⁻¹).



Fig. S7 B3LYP/6-31G (d,p)-optimized geometries of two monomers.



Fig. S8. Representation of the hole-partical wave functions corresponding to the natural transition orbitals (NTOs) at the level of TDDFT/optimized- ω B97x/6-31G (d,p) for the selected important transitions of the dimers.

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