Electronic Supplementary Information

Spectroscopic Readout of Polyoxometalates' Molecular Information via Self-Assembly

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Scheme 1 Synthesis of 1·Br

Fig. S1 UV-Vis absorption spectra of 1·Br in CHCl\textsubscript{3} at 20 \degree C.

Fig. S2 UV-Vis spectra of (Bu\textsubscript{4}N)\textsubscript{4}[SiMo\textsubscript{12}O\textsubscript{40}] and (Bu\textsubscript{4}N)\textsubscript{4}[SiW\textsubscript{12}O\textsubscript{40}] in CH\textsubscript{3}CN (10 \mu M, at 20 \degree C)

Fig. S3 Exciton band structures for one-dimensional assemblies (ref. 15).

Fig. S4 Schematic illustration of exciton band structures for DAS chromophores in (a) (1)\textsubscript{4}[SiMo\textsubscript{12}O\textsubscript{40}] (Fig. 2a) and planar lamellar structure with two molecules per unit cell, (b) (1)\textsubscript{4}[SiW\textsubscript{12}O\textsubscript{40}] (Fig. 2b).

Fig. S5 Temperature dependence of UV-Vis and CD spectra of (a) (1)\textsubscript{4}[SiMo\textsubscript{12}O\textsubscript{40}] and (b) (1)\textsubscript{4}[SiW\textsubscript{12}O\textsubscript{40}].

Fig. S6 (a) Temperature dependence of the absorbance ($A_{509}/A_{579}$) of (1)\textsubscript{4}[SiMo\textsubscript{12}O\textsubscript{40}].

(b) Plot of the absorbance ($A_{477}/A_{543}$) and $[\theta]$ (at 424 and 479 nm) of (1)\textsubscript{4}[SiW\textsubscript{12}O\textsubscript{40}] as a function of temperature.

Fig. S7 Time-course of the absorption spectra of (1)\textsubscript{4}[SiW\textsubscript{12}O\textsubscript{40}] in CHCl\textsubscript{3} (10 \mu M) at 20 \degree C.
Scheme S1. Synthetic route to 1·Br.

Compounds 2-5 were synthesized according to the published procedure.\textsuperscript{S1} The introduction of ether-linkage in the alkylchains has been shown to improve self-assembly characteristics of synthetic lipids and supramolecular assemblies.\textsuperscript{S2}

Synthesis of 6: A solution of 5 (3.00 g, 3.55 mmol) and 4-methylpyridine (992 mg, 10.7 mmol) in EtOH (8 mL) was refluxed for 10 h. After evaporation of the solvent, the crude product was purified by column chromatography on SiO\textsubscript{2} (CHCl\textsubscript{3}/MeOH 4:1, Rf 0.4) to give 6 as a colorless solid (2.34 g, 70%).

\textsuperscript{1}H NMR (300 MHz, CDCl\textsubscript{3}, TMS) \(\delta\) 9.20 (d, \(J = 6.6\) Hz, 2H), 7.86 (d, \(J = 6.6\) Hz, 2H), 7.52 (d, \(J = 6.9\) Hz, 1H), 7.26 (t, \(J = 5.5\) Hz, 1H), 6.89 (t, \(J = 5.5\) Hz, 1H), 4.89 (t, \(J = 7.4\) Hz, 2H), 4.35 (q, \(J = 6.6\) Hz, 1H), 3.51–3.30 (m, 12H), 2.69 (s, 3H), 2.38–2.25 (m, 4H), 2.07–2.00 (m, 4H), 1.81–1.73 (m, 4H), 1.64–1.52 (m, 8H), 1.26 (m, 46H), 0.88 (t, \(J = 6.6\) Hz, 6H).
**Synthesis of 1·Br:** To a solution of 6 (2.31 g, 2.46 mmol) and 4-dimethylaminobenzaldehyde (370 mg, 2.48 mmol) in EtOH (20 mL) was added 3 drops of piperidine and the mixture was refluxed for 12 h. After cooling to room temperature, the resulting solid was collected by filtration and purified by recrystallization from MeOH to give 1·Br as a dark red solid (1.41 g, 54%).

**1H NMR** (300 MHz, CDCl₃, TMS) δ 8.90 (d, J = 6.9 Hz, 2H), 7.84 (d, J = 6.9 Hz, 2H), 7.66 (d, J = 16 Hz, 1H), 7.59 (d, J = 7.0 Hz, 1H), 7.54 (d, J = 9.0 Hz, 2H), 7.24 (t, J = 5.6 Hz, 1H), 6.99 (t, J = 5.6 Hz, 1H), 6.87 (d, J = 16 Hz, 1H), 6.70 (d, J = 9.0 Hz, 2H), 4.67 (t, J = 7.4 Hz, 2H), 4.37 (q, J = 6.7 Hz, 1H), 3.50–3.29 (m, 12H), 3.08 (s, 6H), 2.40–2.27 (m, 4H), 2.11–1.97 (m, 4H), 1.83–1.73 (m, 4H), 1.66–1.54 (m, 8H), 1.25 (m, 46H), 0.88 (t, J = 6.5 Hz, 6H).

**Preparation of 1/POM complexes:** To a solution of (Bu₄N)₄[SiM₁₂O₄₀] (M = Mo, W) in CH₃CN/EtOH (3:1 v/v, 4 mL) was added a solution of 1·Br (4 equiv.) in CH₃CN/EtOH (3:1 v/v, 6 mL) with stirring at room temperature for 30 min. The resulting solid was collected by filtration and washed with CH₃CN/EtOH (3:1 v/v) to give (1)₄[SiM₁₂O₄₀] as a red-orange solid.

Calc. for (1)₄[SiMo₁₂O₄₀]·4H₂O (C₄₄₄H₄₃₂N₂O₆₄SiMo₁₂): C, 50.10; H, 7.44; N, 4.79. Found: C, 49.94; H, 7.36; N, 4.80.

Calc. for (1)₄[SiW₁₂O₄₀]·4H₂O (C₄₄₄H₄₃₂N₂O₆₄SiW₁₂): C, 42.45; H, 6.31; N, 4.06. Found: C, 42.47; H, 6.24; N, 4.11.
**Fig. S1** UV-Vis absorption spectra of $1\cdot\text{Br}$ in CHCl$_3$ at 20 °C. (a) Dependence of the absorbance on the concentration of $1\cdot\text{Br}$. (b) Plot of the absorbance at 498 nm against the corresponding concentration.

**Fig. S2** UV-Vis spectra at 20 °C; (a) $(\text{Bu}_4\text{N})_4[\text{SiMo}_{12}\text{O}_{40}]$ in CH$_3$CN (10 μM), (b) $(\text{Bu}_4\text{N})_4[\text{SiW}_{12}\text{O}_{40}]$ in CH$_3$CN (10 μM) and (c) $1\cdot\text{Br}$ in CHCl$_3$ (40 μM).
According to the molecular exciton theory, exciton splitting energy for a linear aggregate is expressed as a function of centre-to-centre distance between chromophores \( r \), the angle made by the polarization axes of the unit molecule with the line of molecular centers \( \theta \), the number of interacting chromophores \( N \), and the transition moment \( \mu \) for the singlet-singlet transition in the monomeric chromophore (M. Kasha, ref. 15).

\[
\Delta E = 4\left[\frac{(N-1/N) \mu^2}{\mu^3} (1-3\cos^2\theta)\right]
\]

(1)

Where the \((N-1/N)\) value can be approximated by unity if the excitation energy is delocalized among multiple chromophores.\(^{\text{s3}}\) Meanwhile, the parameters \( r \) and \( \theta \) are not obtained for \( 1 \cdot \text{Br}, \) \( (1)_4[\text{SiMo}_{12}\text{O}_{40}] \) and \( (1)_4[\text{SiW}_{12}\text{O}_{40}] \), because of the lack in single crystal X-ray structures.

![Exciton Band Structures](image)

**Fig. S3**  Exciton band structures for one-dimensional assemblies (M. Kasha, ref. 15).

On the other hand, the UV-vis and CD spectral patterns observed in Fig. 2 are not so simple to allow us modeling of present system based on the simplified molecular exciton model and exciton chirality method.\(^{\text{s4,s5}}\) Schematic illustrations of the correlation of UV-vis absorption peaks and expected exciton coupling patterns are shown in Fig. S4. As described in the manuscript, \((1)_4[\text{SiMo}_{12}\text{O}_{40}]\) gave UV-vis spectral maxima at 509 nm and a shoulder at 545 nm (Fig. 2a)
**Fig. S4** Schematic illustration of exciton band structures for DAS chromophores in (a) (I)$_4$[SiMo$_{12}$O$_{40}$] (Fig. 2a) and planar lamellar structure with two molecules per unit cell, (b) (I)$_4$[SiW$_{12}$O$_{40}$] (Fig. 2b).

which are red-shifted compared to monomeric absorption peak of 1·Br (498 nm). The observed spectral shift is accompanied by the exciton-coupled CD pattern (Fig. 2a, bottom), but it is not simply interpreted based on a chiral dimer model.$^{54,55}$ The wavelength at which CD intensity becomes zero in between the positive and negative Cotton effects is observed at 545 nm, which is deviated from the absorption wavelength of monomeric chromophore (498 nm). The presence of such two lower-energy level absorption peaks with a small band splitting (509 and 545 nm) is fitly interpretable by a monomolecular lamella with a tilt molecular packing of two molecules per unit cell (Fig. S4a).$^{56}$

In the case of (I)$_4$[SiW$_{12}$O$_{40}$], intramolecular CT absorption bands were observed at 452 and 516 nm (Fig. 2b). These spectral peaks are blue- and red-shifted compared to the monomeric absorption band of 1·Br (498 nm), respectively. This spectral splitting is indicative of the presence of two non-translational chromophore orientations in a unit cell of linear aggregates (oblique molecular orientation, Fig. S3c). On the other hand, the presence of an additional shoulder peak at 543 nm (Fig. 2b) indicates that this UV-vis spectrum is also not simply interpretable by the linear aggregate model (M. Kasha, ref. 15 in the manuscript). This complex spectral pattern could be obtained by assuming exciton interactions occurring among multiple (more than three), non-translationally oriented DAS
chromophores self-assembled at the solvophobic interface consisted of DAS chromophores and [SiW$_{12}$O$_{40}$]$^{4-}$, as schematically shown in Fig. 3b.

Thus, the unique UV-vis and CD spectral characteristics observed for (1)$_4$[SiMo$_{12}$O$_{40}$] and (1)$_4$[SiW$_{12}$O$_{40}$] indicate that exciton interactions among DAS chromophores are not explicable by simple linear interaction model. Rather, DAS chromophores assume translationally non-equivalent molecular orientations, which were induced by interactions with [Si$M_{12}$O$_{40}$]$^{4-}$ ($M$ = Mo, W) anions.

**Fig. S5** Temperature dependence of UV-Vis and CD spectra of (a) (1)$_4$[SiMo$_{12}$O$_{40}$] and (b) (1)$_4$[SiW$_{12}$O$_{40}$]. Arrows indicate changes upon increasing temperature from 20 to 60 °C.
Fig. S6  (a) Temperature dependence of the absorbance ($A_{509}/A_{579}$) of (1)$_4$[SiMo$_{12}$O$_{40}$]. (b) Plot of the absorbance ($A_{477}/A_{543}$) and $\theta$ (at 424 and 479 nm) of (1)$_4$[SiW$_{12}$O$_{40}$] as a function of temperature.

Fig. S7  Time-course of the absorption spectra of (1)$_4$[SiW$_{12}$O$_{40}$] in CHCl$_3$ (10 $\mu$M) at 20 °C. The spectral change was recorded at 20 °C after heating the solution to 60 °C.
References


