

Electronic Supplementary Information (ESI) for

Structure-distortion-induced photomagnetic effect in azobenzene/polyoxometalate Langmuir–Blodgett Films

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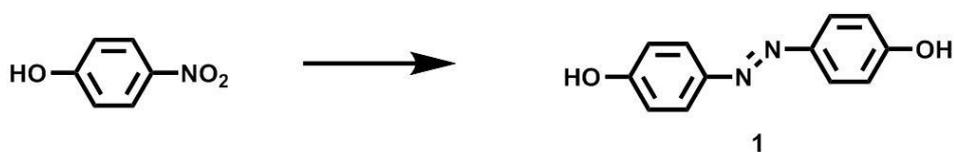
1. Synthesis of material

All reagents were commercially available and used as received.

1.1. Amphiphilic azobenzene (AZ)

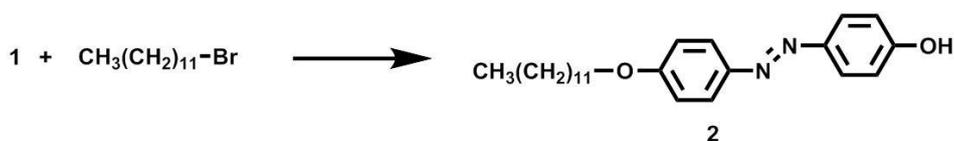
An amphiphilic azobenzene compound was synthesized according to previous reports.^{1,2}

Step 1:



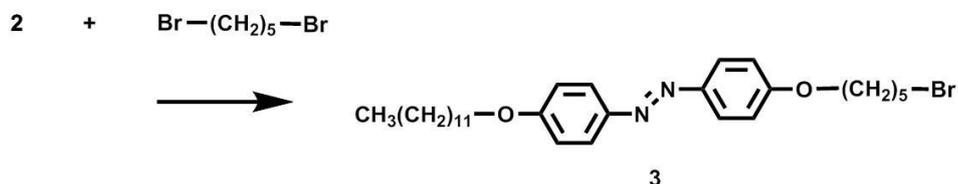
A mixture of *p*-nitrophenol (10.0 g, 72 mmol), KOH (50.0 g, 890 mmol), and water (10 mL) was heated to 120 °C for 1 h, and 200 °C for 3 h. After cooling down, products were dissolved in water. A solution was acidified to pH 1 with concentrated HCl and extracted with diethylether and dried over Na₂SO₄. Diethylether was evaporated, and residue was recrystallized from ethanol–water (1:1 in volume) to give **1** (4.00 g, 19 % yield). ¹H NMR (400 MHz, CD₃OD): δ 7.73 (d, *J* = 8.8, 4H), 6.88 (d, *J* = 8.8, 4H), 4.85 (s, 1H).

Step 2:



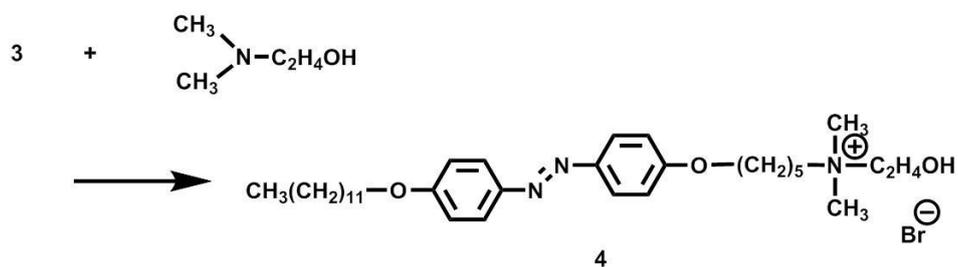
To a solution of **1** (1.07 g, 5 mmol) and dodecylbromide (1.50 g, 6 mmol) in acetone (100 mL), potassium carbonate (1.03 g, 7.5 mmol) was added and refluxed for 6 h. After neutralized with a diluted HCl, the reaction mixture was extracted with CHCl₃ and dried over Na₂SO₄. CHCl₃ was evaporated, and the residue was purified by chromatography on silica gel (eluent: CHCl₃–EtOAc = 40 :1, *R_f* = 0.2) gave **2** (0.574 g, 30 % yield). ¹H NMR (400 MHz, CDCl₃): δ 7.85 (d, *J* = 8.4, 2H), 7.83 (t, *J* = 8.8, 2H), 6.96 (d, *J* = 8.8, 2H), 6.93 (d, *J* = 8.4, 2H), 5.31 (s, 1H), 4.03 (t, *J* = 6.4, 2H), 1.81 (m, 2H), 1.26 (br, 18H), 0.88 (t, *J* = 6.8, 3H).

Step 3:



To a solution of **2** (0.383 g, 1 mmol) and 1,6-dibromopentane (1.22 g, 5 mmol) in ethanol (40 mL), potassium hydroxide (0.0561 g, 1 mmol) was added and refluxed for 6 h. After cooling to room temperature, the precipitate was filtered off. Recrystallization from benzene–ethanol gave **3** (0.289 g, 53 % yield). $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.87 (d, $J = 8.8$, 2H), 7.86 (t, $J = 8.8$, 2H), 7.00 (d, $J = 8.8$, 2H), 6.99 (d, $J = 8.8$, 2H), 4.19 (t, $J = 5.8$, 2H), 4.03 (t, $J = 6.6$, 2H), 3.63 (t, $J = 6.4$, 2H), 1.80 (t, $J = 6.2$, 4H), 1.26 (br, 22H), 0.87 (t, $J = 6.8$, 3H).

Step 4:



To a solution of **2** (0.273 g, 0.5 mmol) in toluene (30 mL), dimethylethanolamine (2.67 g, 15 mmol) was added and refluxed for 70 h. After cooling to room temperature, the precipitate was filtered off. Recrystallization from ethanol–benzene gave **4** (0.190 g, 60 % yield). $^1\text{H NMR}$ (400 MHz, CD_3OD): δ 7.83 (d, $J = 9.2$, 2H), 7.82 (t, $J = 9.2$, 2H), 7.04 (d, $J = 8.8$, 2H), 7.03 (d, $J = 8.8$, 2H), 4.11 (t, $J = 6.4$, 2H), 4.06 (t, $J = 6.4$, 2H), 3.99 (br, 1H), 3.47 (m, 2H), 3.30 (s, 6H), 1.80 (m, 4H), 1.26 (br, 26H), 0.89 (t, $J = 6.8$, 3H).

1.2. Magnetic polyoxometalate (Co–POM)

A magnetic polyoxometalate was synthesized according to previous reports.³

$\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ (30.0 g) was dissolved in H_2O (37 mL). Then, 85 % H_3PO_4 (0.75 mL) followed by glacial acetic acid (5.5 mL) was added to the stirring solution. The white precipitate was filtered off and dried at 140 °C for 2 h to give **5** (18 g). FT-IR (KBr): ν 1163 (P=O stretching); 1058, 1013, 994 (P–O stretching); 938 (W–O stretching); 889, 816, 748 (W–O stretching, bridge mode).

To a solution of $\text{Co}(\text{NO}_3) \cdot 6\text{H}_2\text{O}$ (0.41 g) in H_2O (30 mL), compound **5** (2.0 g) was added and heated until a homogeneous purple to burgundy solution obtained. Excess KCl (6.0 g) was added, and cooled to room temperature. The blue-purple precipitate was filtered off. The crude compound was dissolved in hot H_2O (10 mL) and stand overnight at 5 °C. A crystalline blue-purple solid was collected and dried at 80 °C under vacuum for 2 h to give the product (1.0 g). FT-IR (KBr): ν 1032 (P–O stretching); 937 (W–O stretching); 882, 800, 725 (W–O stretching, bridge mode).

2. FT-IR dichroism spectroscopy

A linear FT-IR dichroism measurement was performed to estimate AZ orientation. As a result, AZ tilts 46° from the surface normal, which agree well with the value obtained from UV-Vis measurements.

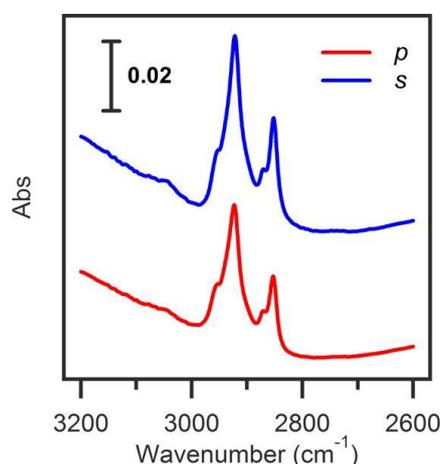


Fig. S1 Linear FT-IR dichroism spectra for (AZ/Co–POM) films: (red) *p*-polarized and (blue) *s*-polarized spectrum. 300 Co–POM layers were transferred onto each side of a CaF_2 substrate.

3. Model Langmuir–Blodgett Film

In order to check whether Co-POM exhibits photochromism, we have prepared the model Langmuir-Blodgett films by using a dioctadecyldimethylammonium cation (DODA), instead of AZ.

3.1. Film Preparation

DODA was dissolved in CHCl_3 to prepare a solution at 1.0 mM. The solution was spread on a subphase of Co-POM aqueous solution (1.0 μM) at room temperature. A floating monolayer of DODA was hybridized with Co-POM at the air-water interface. Fifteen minutes later, the floating hybrid monolayers were compressed up to a surface pressure of 30 mN m^{-1} . After 30 min, the floating hybrid monolayers were transferred onto a hydrophilic substrate by a vertical dipping method with the speed of 10 mm min^{-1} . Langmuir-Blodgett films composed of DODA and Co-POM were prepared by repeating this cycle. The transfer ratio was found to be 0.9–1.0, indicating an ideal transfer.

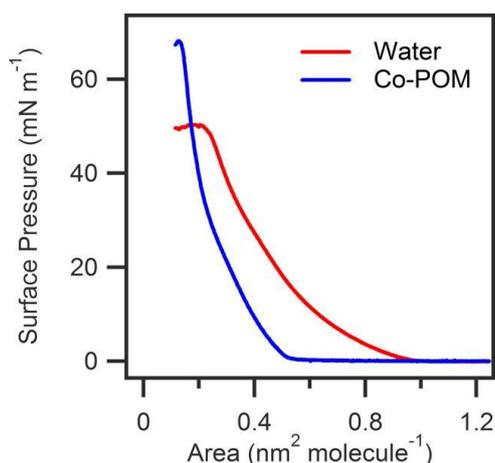


Fig. S2 Surface pressure–area (π -A) isotherms of DODA at the air–water interface: (red) on pure water and (blue) on Co-POM aqueous solution (1.0 μM).

3.2. Structure

XRD patterns showed three diffraction peaks at $2\theta = 1.85, 3.66,$ and 5.31° . These peaks are ascribed to the (001), (002), and (003) reflections from Co-POM layer, respectively. Thus, LB films obviously possess the layered structure and, from the (001) diffraction peak, the basal spacing of the unit layer (DODA/Co-POM/DODA) is calculated to be 47.6 \AA .

A linear FT-IR dichroism measurement was performed to estimate DODA orientation. By using the absorption at 2925 cm^{-1} (CH_2 antisymmetric stretching) as a guide, DODA is revealed to tilt 46° from the surface normal.

Therefore, structure of the DODA LB films is similar to that of AZ LB films.

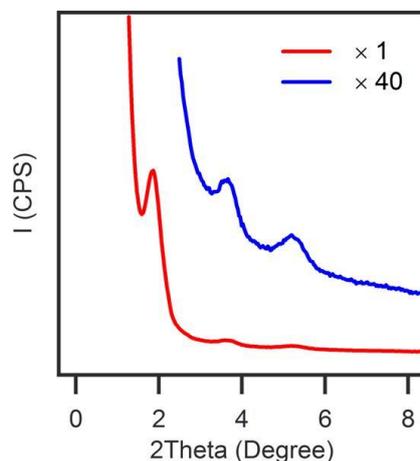


Fig. S3 XRD patterns for (DODA/Co-POM) films. 300 Co-POM layers were transferred onto each side of a quartz substrate.

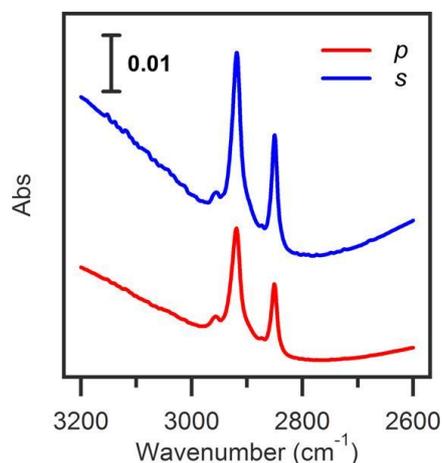


Fig. S4 Linear FT-IR dichroism spectra for (DODA/Co-POM) films: (red) p -polarized and (blue) s -polarized spectrum. 300 Co-POM layers were transferred onto each side of a CaF_2 substrate.

3.3. Photoresponse

UV irradiation was performed to DODA LB films in order to check whether Co-POM exhibits photochromism. As a result, we could not observe any spectral change in DODA LB films. Therefore, it is concluded that Co-POM does not exhibit photochromism.

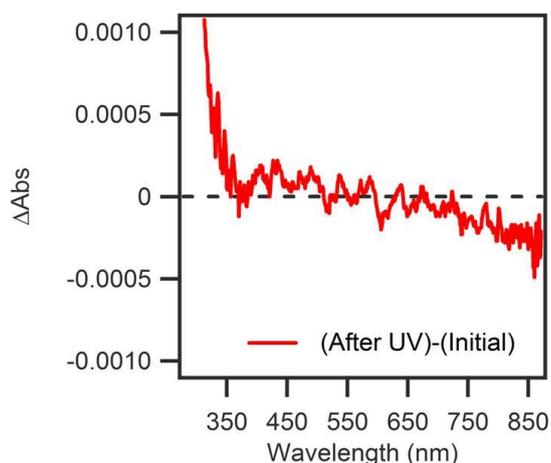


Fig. S5 UV-Vis absorption spectra for (DODA/Co-POM) films upon UV irradiation at room temperature. If Co-POM exhibits photochromism upon excitation of a ligand-to-metal charge transfer (LMCT; oxygen to W^{VI} ion) band, W^{VI} ions are reduced to form mixed-valence species, leading to exhibit an intervalence charge transfer (IVCT) band between 600 and 900 nm. However, we could not observe changes in visible region. Therefore, photochromism of DODA is ruled out. 300 Co-POM layers were transferred onto each side of a quartz substrate.

4. References

1. T. Kunitake, Y. Okahata, M. Shimomura, S. Yamanuki and K. Takarabe, *J. Am. Chem. Soc.*, 1981, **103**, 5401.
2. W.-H. Wei, T. Tomohiro, M. Kodaka and H. Okuno, *J. Org. Chem.*, 2006, **65**, 8979.
3. R. G. Finke, M. W. Droege and P. J. Domaille, *Inorg. Chem.*, 1987, **26**, 3886.