Electronic Supplementary Information

Exciton Dissociation in Quantum Dots Connected with Photochromic Molecule Bridges

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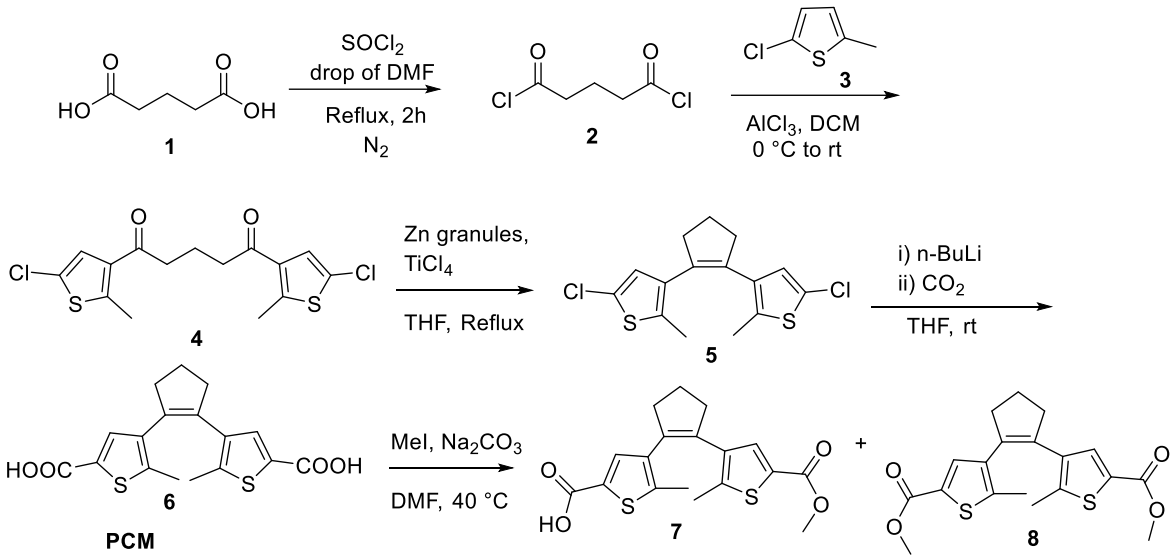


Scheme S1. Synthesis of photochromic compound **6** and **7**.

Synthesis of compound 2:

Glutaric acid **1** (200.0 mg, 1.51 mmol, 1.0 equiv.) and thionyl chloride (5 mL) along with a drop of DMF were added to a nitrogen flushed 50 mL round bottom flask (RBF) and refluxed for 3 h to form the intermediate acid chloride **2**, as indicated by ^{1}H NMR spectrum. The reaction was further refluxed for 30 min and directly taken to the next step. In a later scaled up reaction, 1.0 g of glutaric acid **1**, 5.0 mL of thionyl chloride and 3 drops of DMF were used and the reaction was refluxed for 5 h to achieve full conversion to the acid chloride **2**.

Synthesis of compound 4:[1]

To a stirring mixture of an ice-cooled solution of dry $AlCl_3$ powder (605.5 mg, 4.54 mmol, 3.0 equiv.) in DCM (6.0 mL), glutaryl chloride **2** (255.8 mg, 1.51 mmol, 1.0 equiv.) and 2-Chloro-5-methylthiophene **3** (0.35 mL, 3.18 mmol, 2.1 equiv.) were added dropwise sequentially. The reaction mixture was stirred for 3 h at RT, until the mixture turned dark red. A mixture of concentrated HCl (4.0 mL) and ice (6.0 g) was carefully added to the reaction flask. The water layer was extracted with DCM (3 × 10.0 mL). The combined organic phase was washed with saturated sodium bicarbonate solution (6.0 mL), water (5.0 mL) and saturated NaCl solution (5.0 mL). The organic layer was then dried using anhydrous Na_2SO_4 and filtered. The solvent was evaporated using a rotavap under reduced pressure to yield a brown viscous liquid. The crude product was further purified by 3% EtOAc in hexanes to obtain the desired product as a white solid, in 84% (458.0 mg) yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18 (s, 2H), 2.86 (t, J = 6.9 Hz, 4H), 2.66 (s, 6H), 2.09 – 2.03 (m, 2H).

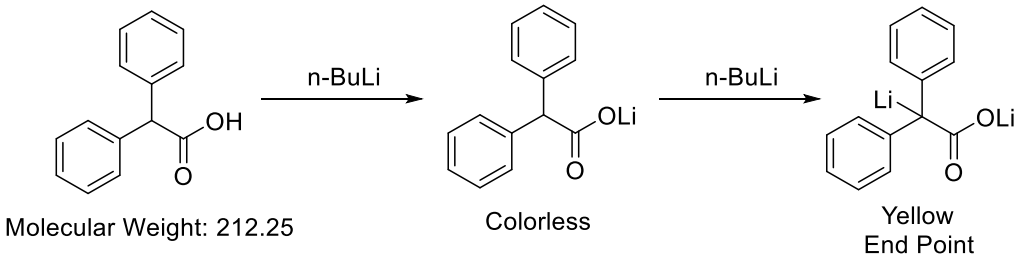
Synthesis of compound 5:[1]

A mixture of $TiCl_4$ (0.15 mL, 1.38 mmol, 2.5 equiv.), Zn granules (434.4 mg, 6.64 mmol, 12.0 equiv.) and THF (10 mL) was added to a round bottom flask under nitrogen, the mixture was stirred at refluxing condition for 1h. The mixture was cooled to 0 °C, and compound **4** (200.0 mg, 0.55 mmol, 1.0 equiv.) dissolved in 2 mL THF was added. The mixture was refluxed for 14 h after which a full conversion was observed. The reaction mixture was then quenched with two drops of saturated aqueous K_2CO_3 and passed through celite and washed with EtOAc (20 mL x 3). The combined organic layer was washed with H_2O (20.0 mL), followed by saturated $NaHCO_3$ (20.0 mL) and then dried over anhydrous Na_2SO_4 and filtered. The solvent was removed using a rotavap under reduced pressure. Further purification was done using flash column chromatography using hexane as the eluent, the desired product was obtained as a white solid in 76% (139 mg) yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.57 (s, 2H), 2.71 (t, J = 7.5 Hz, 4H), 2.06 – 1.98 (m, 2H), 1.89 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 134.8, 134.4, 133.3, 126.7, 125.2, 38.3, 22.8.

Synthesis of compound 6 (PCM):[2]

Compound **5** (500.0 mg, 1.52 mmol, 1.0 equiv.) was dissolved in anhydrous THF (20.0 mL) in a round bottom flask equipped with drying tube and nitrogen atmosphere. To this solution, *n*-BuLi (4.0 mL, 0.94 M in hexanes, ACROS, 2.5 equiv.) was added. After a yellowish slurry was obtained, it was further stirred for 1 h. Then, excess CO_2 solid was added to the flask and the mixture was stirred for 45 min. The reaction mixture (still cold with CO_2 solid) was quenched by adding H_2O (10.0 mL) dropwise. The aqueous layer was acidified to pH = 1 with 2 M HCl and extracted with DCM (3 x 25 mL). The organic layer was washed with H_2O (30 mL) and dried over Na_2SO_4. The organic layer was filtered and concentrated to obtain a brown slurry. The crude product was purified by flash column chromatography using solvent system of hexanes/DCM to 2% MeOH/DCM to obtain a light brown solid as the desired product in 56% (296 mg) yield. ^{1}H NMR (400 MHz, d_6-DMSO) δ 7.40 (s, 2H), 2.77 (t, J = 7.5 Hz, 4H), 2.05 – 1.97 (m, 2H), 1.92 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.7, 141.8, 136.5, 134.4, 139.9, 130.5, 37.9, 22.4, 14.4.

The concentration of *n*-butyl lithium was determined prior to reaction by the following method in Scheme S2.



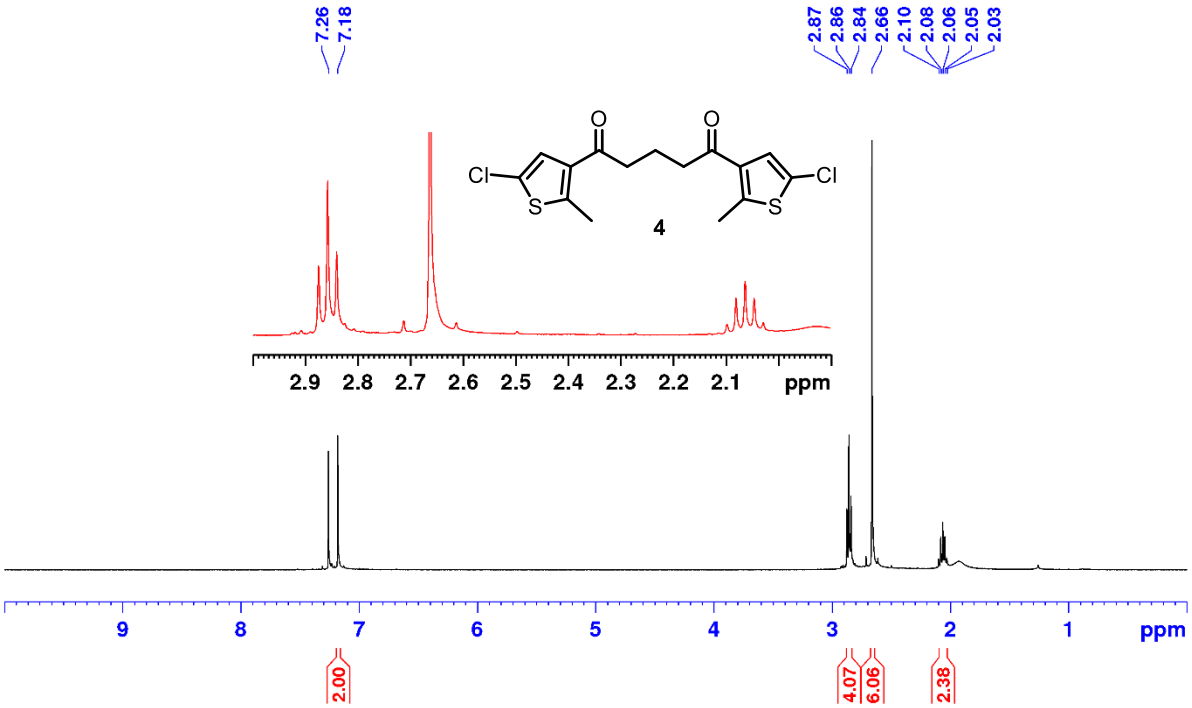
Scheme S2. Titration reaction for n-BuLi concentration determination.

Diphenylacetic acid (50.0 mg, 0.235 mmol, 1 equiv.) was added to a dried scintillation vial under N_2 atmosphere. Anhydrous THF (1.0 mL) was added to the scintillation vial. 700 µL of 1.6 N *n*-butyl lithium solution in hexanes was added slowly. The n-butyl lithium solution was added until the solution in the vial turned deep yellow. At the end of the titration, 450 µL of the *n*-butyl lithium solution remained in the syringe. The titration required 250 µL of the n-butyl lithium solution. The concentration of the n-BuLi was calculated using the following formula:

$$\frac{0.235\ mmole\ Diphenylacetic\ acid}{0.250\ mL} = 0.94\ M$$

Synthesis of compound 7 (mono-esterified PCM):[3]

A mixture of compound **6** (100.0 mg, 0.29 mmol, 1.0 equiv.), DMF (5.0 mL), and Na_2CO_3 (121.7 mg, 1.15 mmol, 4.0 equiv.) was stirred for 30 min at rt. To this solution, CH_3I (19.6 µL, 0.29 mmol, 1.0 equiv.) was added dropwise and the mixture was stirred for 2 hr at 40 °C. The reaction was then stopped and DMF was removed under vacuum, the residue was diluted with H_2O and acidified with 2 M HCl solution (~pH 2). The aqueous layer was then extracted with DCM (10 mL X 2). The combined organic layer was washed with H_2O (20 mL) to remove residual DMF, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude product was then purified by using flash chromatography (DCM to 1% MeOH/DCM) to afford a brown solid as the desired monoester **7** in 22% yield (23 mg, 0.063 mmol). The dimethyl ester byproduct **8** was also isolated in 27 mg (0.072 mmol, 50% yield based on CH_3I). R_f = 0.29 in 5% MeOH/DCM for compound **7**. m.p. 172.0-174.0 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (s, 1H), 7.50 (s, 1H), 3.84 (s, 3H), 2.79 (t, J = 7.4 Hz, 4H), 2.08 (m, J = 7.5 Hz, 2H), 1.94 (s, 3H), 1.92 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.5, 162.5, 144.6, 142.7, 137.0, 136.5, 135.9, 135.1, 134.6, 134.4, 129.4, 128.4, 52.0, 38.63, 38.61, 22.8, 14.9, 14.8.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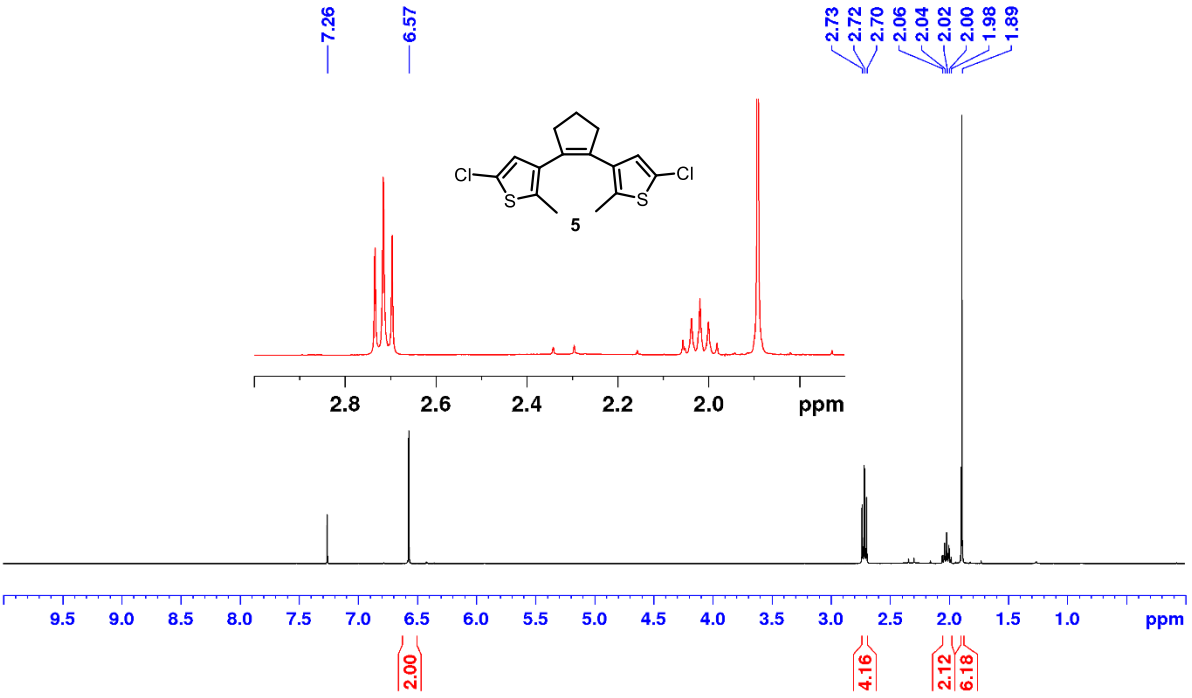
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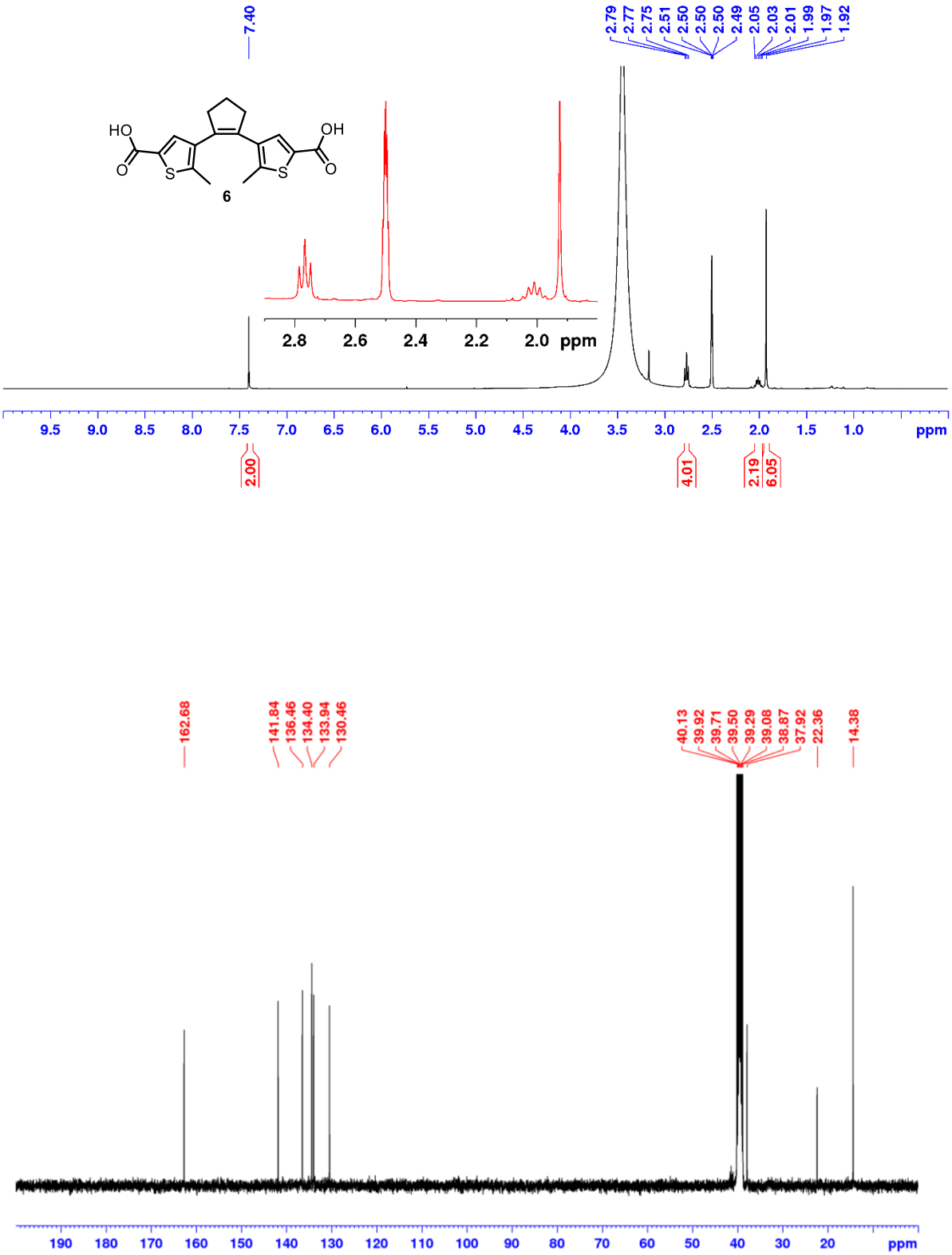

Fig. S1 ^{1}H and ^{13}C NMR spectra of intermediates and compound **6** (PCM) in DMSO-d_6.

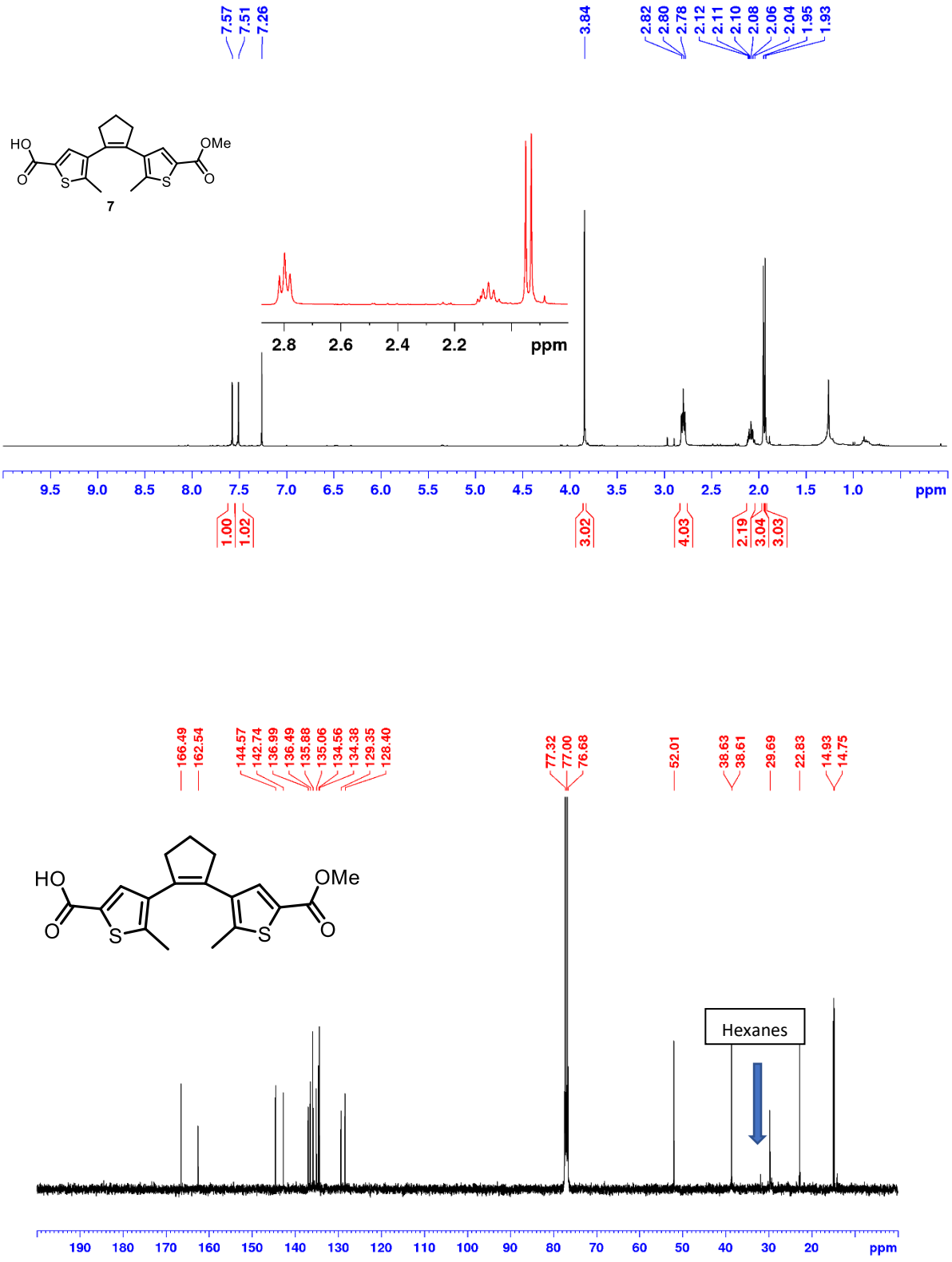

Fig. S2 ^{1}H and ^{13}C NMR spectra of compound **7** in $CDCl_3$

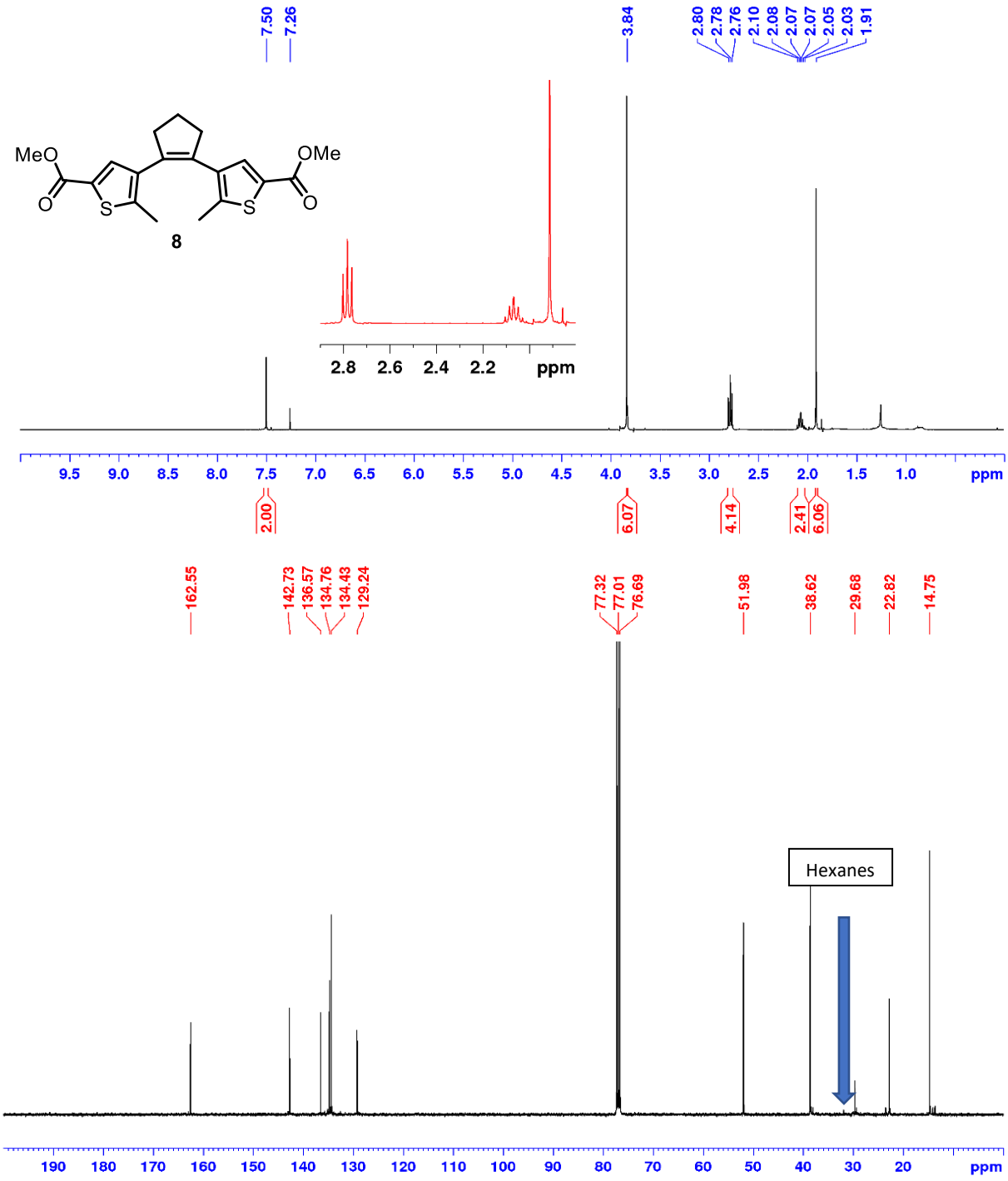

Fig. S3 ^{1}H and ^{13}C NMR spectra of compound **8** in $CDCl_3$

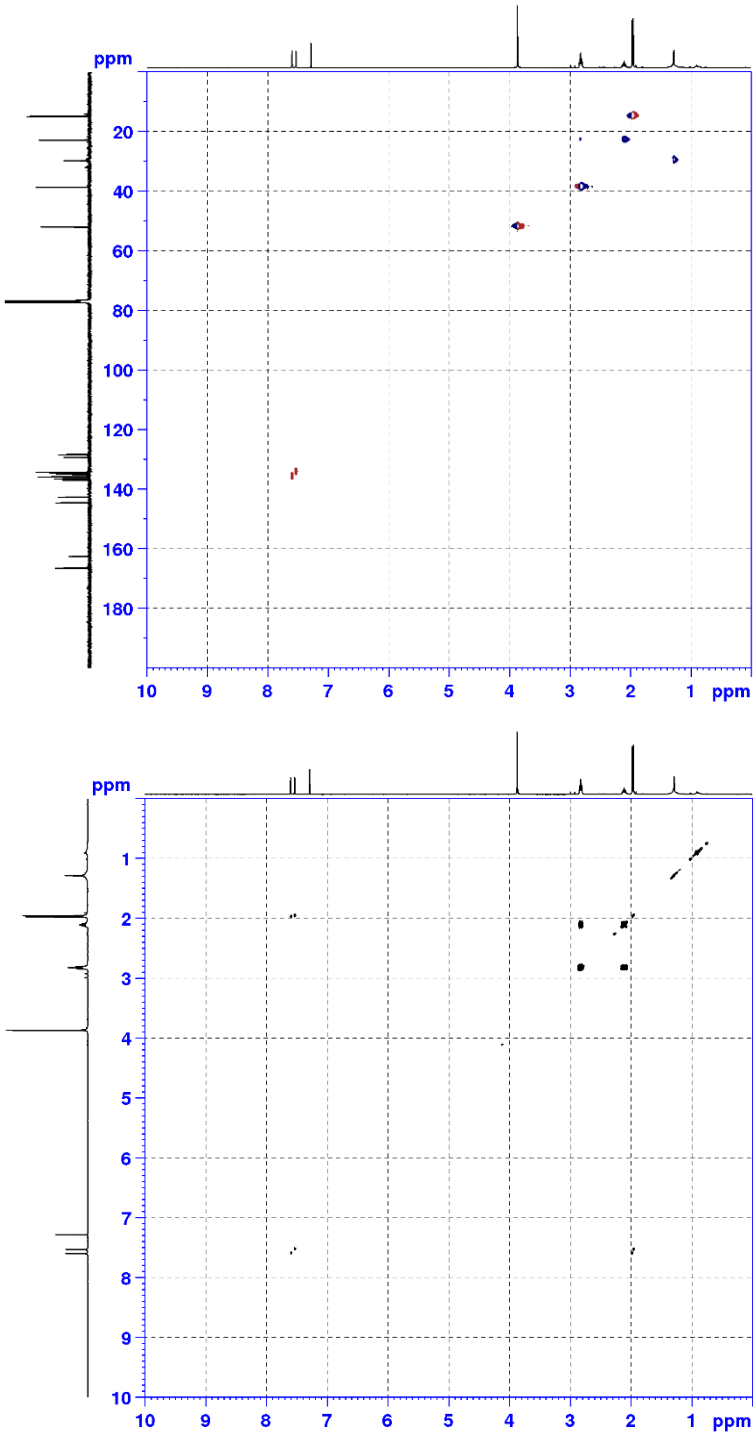

Fig. S4 HSQC and COSY NMR spectra of compound **7** in $CDCl_3$

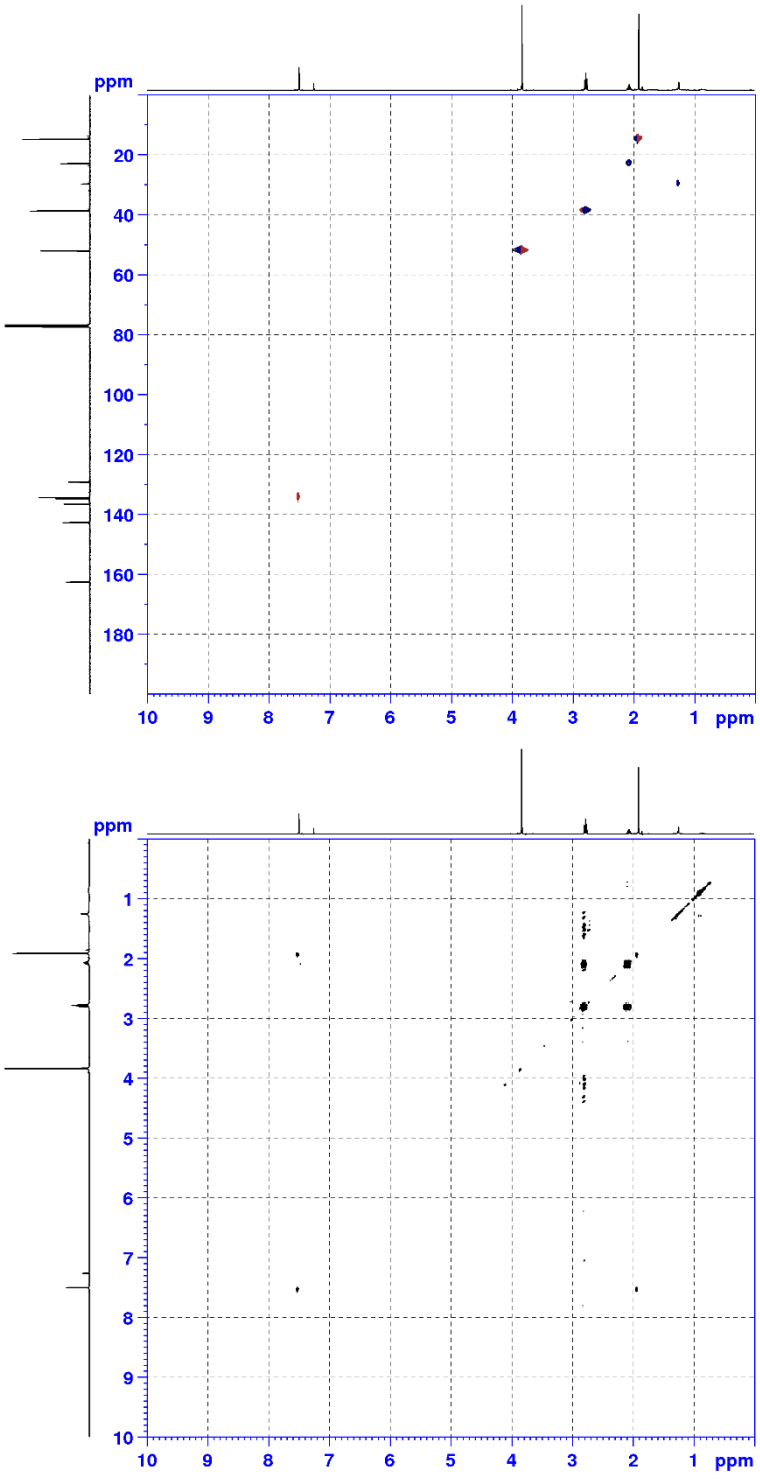

Fig. S5 HSQC and COSY NMR spectra of compound **8** in $CDCl_3$

Raman spectra for probing ligand exchange on PCM treated QD films

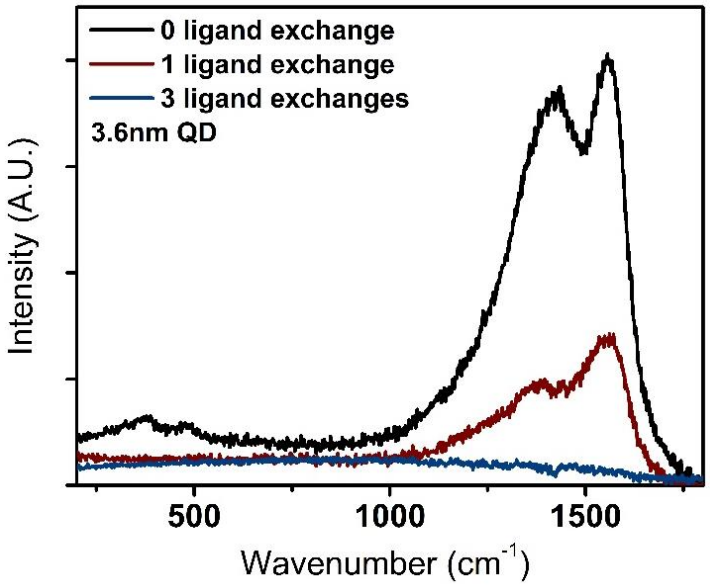

Fig. S6 Raman spectra of QD thin film samples with different number of ligand exchange treatment with PCM

Absorbance spectra of PCM bridged 3.6nm QD assembly with closed and open PCM state

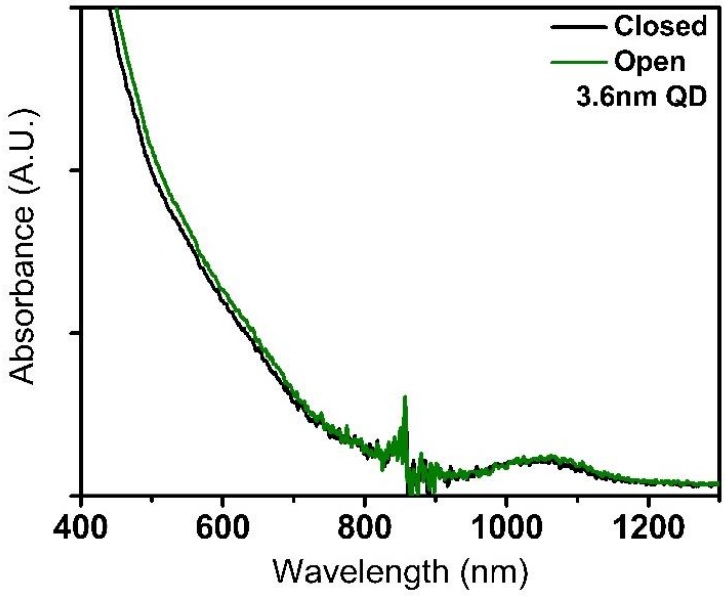

Fig. S7 Absorbance spectra of 3.6 nm QD assembly with "closed" PCM (black) and "open" PCM (green).

GISAXS scattering images and integrated intensity plots of 2.9 nm QD films with a closed and open PCM state

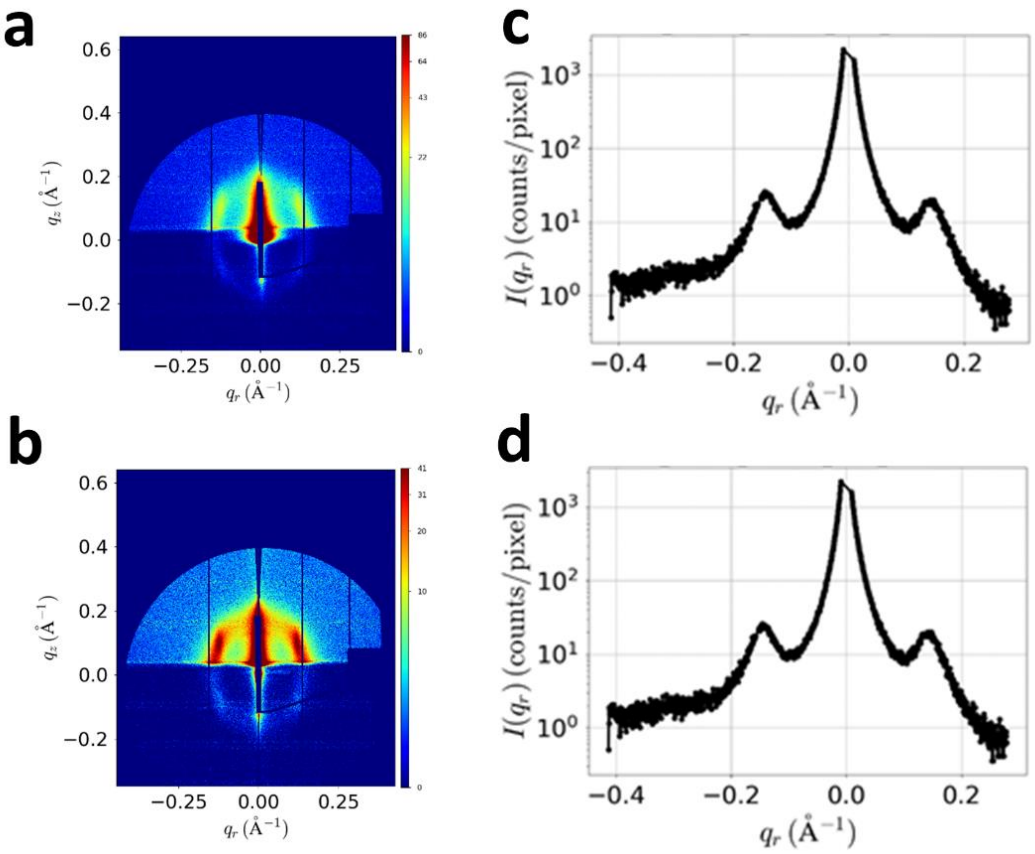

Fig. S8 The GISAXS patterns of 2.9nm QD samples with (a) "closed" PCM state and (b) "open" PCM state and the integrated intensity plots as a function of reciprocal-space of (c) "closed" PCM state and (d) "open" PCM state. These results were obtained using x-ray beam incident angle of 0.20˚.

QD size	PCM – "Closed" state Average Inter-QD Distance	PCM – "Open" state Average Inter-QD Distance
2.9 nm	43.8 Å	45.2 Å
3.6 nm	48.7 Å	48.0 Å
4.7 nm	64.7 Å	65.9 Å

Table S1 Inter-QD distance values obtained from GISAXS measurement. The displayed values are the average of the values obtained by measurements using an X-ray incident angle from 0.10 to 0.25˚.

Absorbance spectra of mono-esterified PCM (compound 7) in MeOH

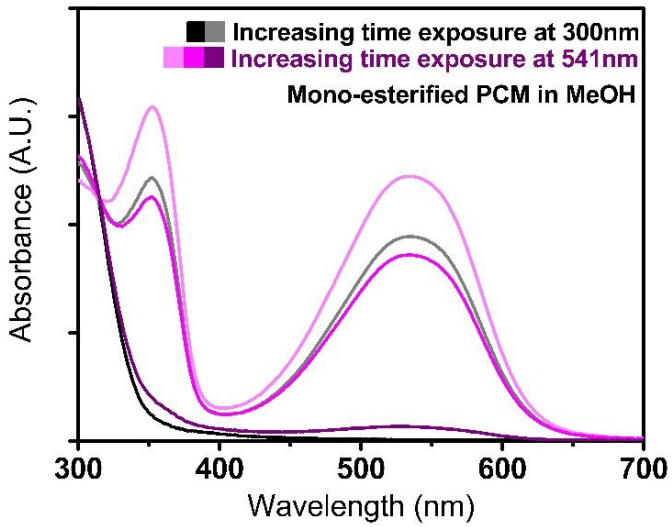

Fig. S9 Absorbance spectra of mono-esterified PCM (compound **7**) in MeOH after light exposure at 541 nm (magenta) and 300 nm (gray). The absorbance peak locations (350 nm and 537 nm) responsible for the "open" state closely resemble those observed in the PCM (compound **6**) in Figure 2(a).

PL cycle of PCMs treated 3.6 nm QD solution sample

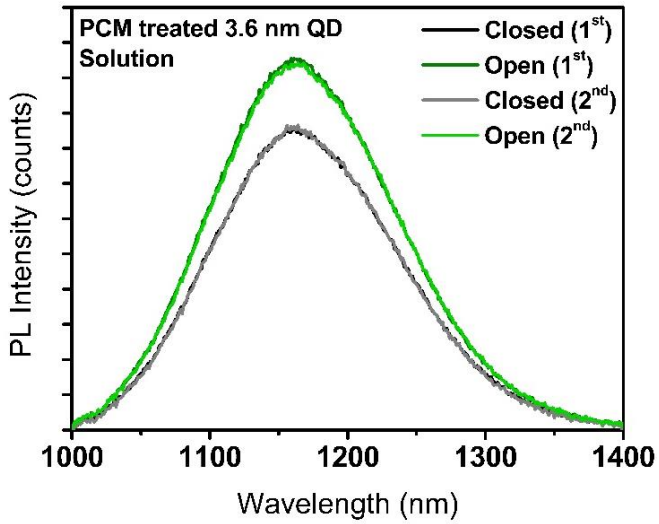

Fig. S10 PL spectra of PCM (compound **6**) treated 3.6 nm QD solution. While the identical molar ratio of mono-esterified PCM (compound **7**) to QD solution does not show any noticeable PL switching response as shown in Figure 5, the PCM (compound **6**) treated QD solution shows switchable PL intensity differences upon PCM configuration change.

References

1. C. Yu, B. Hu, C. Liu and J. Li, *J. Phys. Org. Chem.*, 2017, **30**, e3584.
2. L. N. Lucas, J. J. de Jong, J. H. van Esch, R. M. Kellogg and B. L. Feringa, *Eur. J. Org. Chem.*, 2003, **2003**, 155-166.
3. K. Zheng, H. Wang and H.-F. Chow, *Org. Biomol. Chem.*, 2019, **17**, 3285-3291.