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Electronic Supplemental Information

Photoluminescence Switching in Quantum Dots Connected with Fluorinated and Hydrogenated Photochromic Molecules

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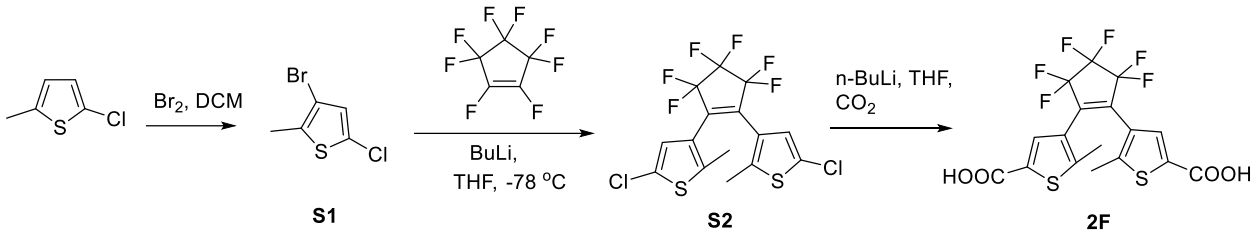
Syntheses for molecules 1H and 2F are based on those provided eariler in liturature. [1,2] Detailed Synthesis for molecule 1H and information for the mono-esterified version of 1H are presented in the supporting information of the work by Yoon et. al. [3]. The following is information for the synthesis of molecule 2F.

Synthesis of compound 2F:



Scheme S1 Synthesis of compound **2F**

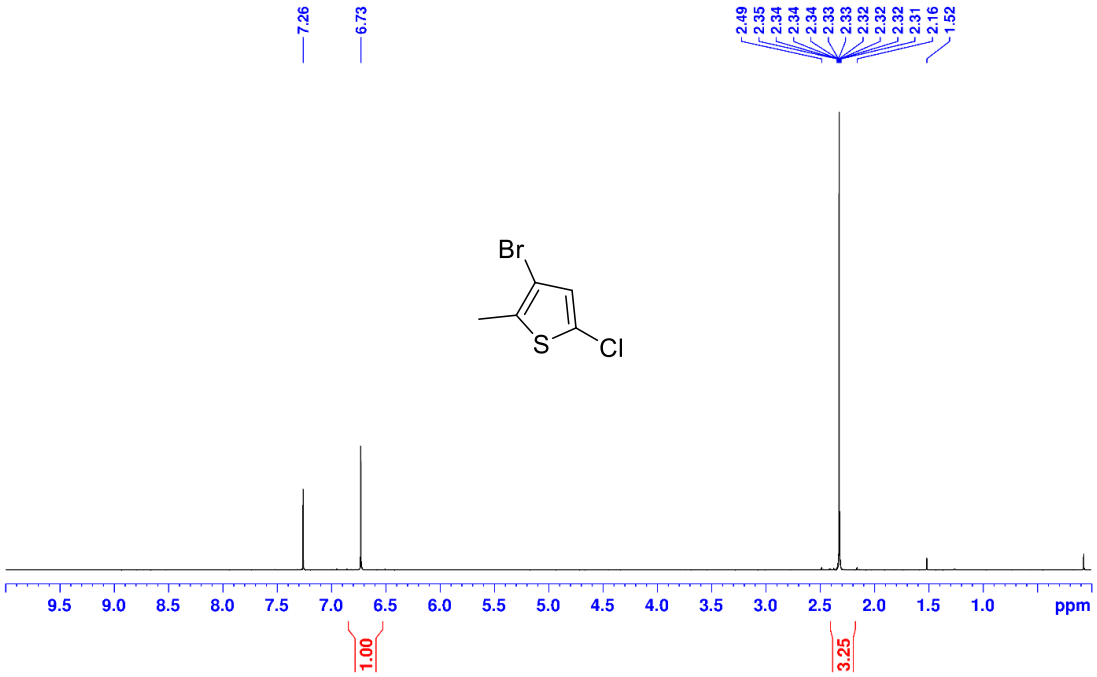
Synthesis of compound S1. 2-chloro-5-methylthiophene (5 g, 37.70 mmol, 1 equiv) was dissolved in DCM (10 mL) in a dried and nitrogen flushed round-bottomed flask. The temperature was reduced to 0 °C via an ice bath. Bromine (2.2 mL, 41.47 mmol, 1.1 equiv) was added dropwise over 15 minutes. The reaction mixture was stirred at 0 °C for two hours, at which point ^{1}HNMR showed full conversion to the desired product. The reaction was quenched with 5 mL of saturated $NaHCO_3$ solution. DI water (10 mL) was added to the reaction mixture and the layers were separated. The aqueous layer was extracted with DCM (10 mL x 3). The organic layers were combined, washed with DI water (10 mL x 2), dried over Na_2SO_4, filtered and the solvent was removed under reduced pressure. The crude product was a yellowish-orange liquid. The liquid was subjected to short path distillation at 160 °C. Then the clear liquid was obtained. Then it was further purified using column chromatography using pure hexanes to obtain clear liquid as a desired product in 6.193 g (77.6%). (R_f = 0.8 in Hexane).; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.72 (s, 1H), 2.33(s, 3H); ^{13}C NMR (400 MHz, $CDCl_3$) δ 133.2, 128.4, 126.8, 107.5, 14.7.

Synthesis of compound S2. 4-Bromo-2-chloro-5-methylthiophene **S1** (1.001 g, 4.73 mmol, 3.0 equiv) was dissolved in anhydrous diethylether 10 mL in a flame dried round bottom flask at -78 °C. N-butyl lithium (5.52 mmol, 3.5 equiv) was added to the reaction mixture and left for half an hour. Then octafluorocyclopentene (1.58 mmol, 1 equiv) was added to the mixture and stirred at the same temperature for 60 minutes. The mixture was warmed to room temperature and left for 3 h. Then reaction was quenched with 1.0 M HCl (10 mL). The aqueous layer was extracted with diethyl ether. The crude was further purified using column chromatography to obtain white solid in 414 mg, 59.9% yield. (R_f = 0.79 in Hexane).; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.90 (s, 1H), 1.92(s, 3H).

Synthesis of compound 2F. Compound **S2** (200 mg, 0.46 mmol, 1.0 equiv) was dissolved in anhydrous diethyl ether (5 mL) and added to a flame dried flask at 0 °C. n-Butyl lithium (1.15 mmol, 2.5 equiv) was added to the reaction mixture, and left stirring for 30 minutes. In another flask dry ice was added, then the reaction mixture was transferred to the flask with dry ice and stirred for 75 min. The reaction was quenched with 2 M HCl (10 mL). The aqueous layer was extracted using DCM 20 mL (10 × 2). The crude was further purified using column chromatography 0-1.5% MeOH/DCM to obtain white solid, 94.1 mg 44.8% yield. (R_f = 0.48 in 3% MeOH/DCM with 0.5% AcOH).; ^{1}H NMR (400 MHz, d_6-DMSO) δ 13.39 (s, 1H), 7.67 (s, 1H),

1.97 (s, 3H); ^{13}C NMR (400 MHz, d$_6$-DMSO) δ 161.9, 148.6, 135.9 (m), 133.3, 132.2, 124.4, 118.1 (m), 115.6 (m), 113.0 (m), 14.3. (m: multiple peaks due to coupling with F)

^{1}H and ^{13}C NMR Spectra:



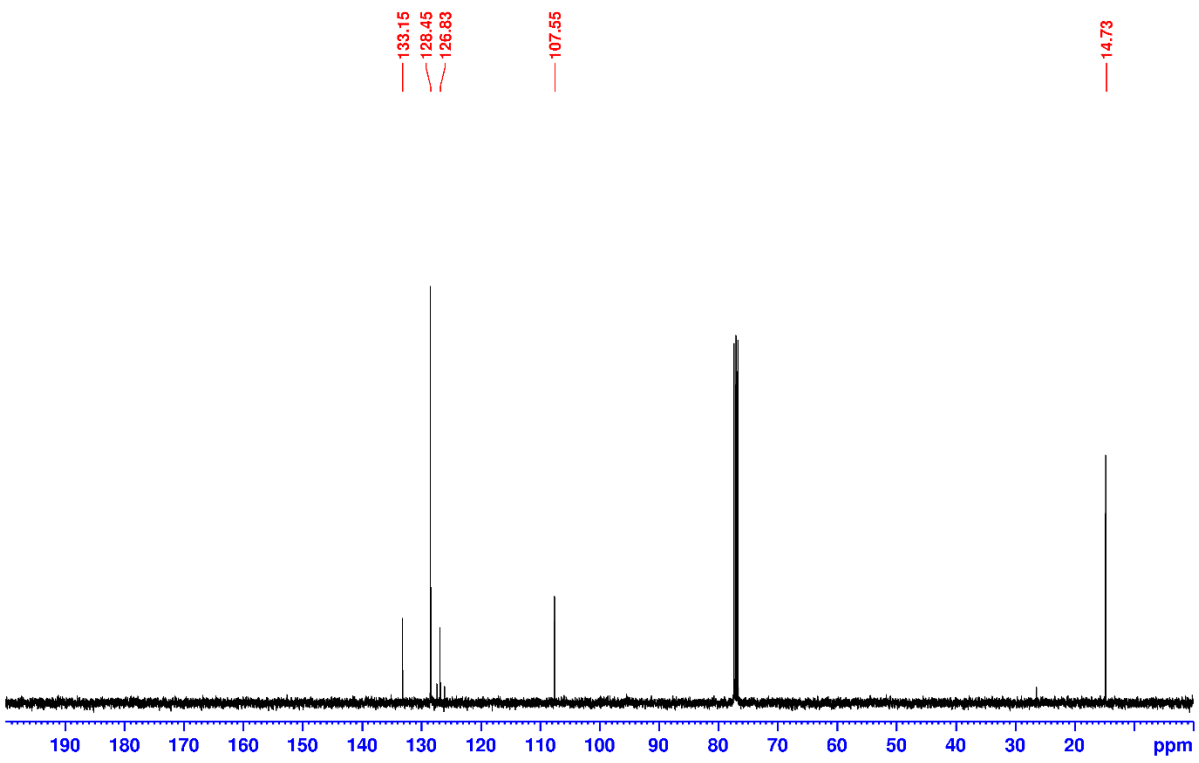


Fig. S1 ^{1}H and ^{13}C NMR spectra of compound **S1** in $CDCl_3$.

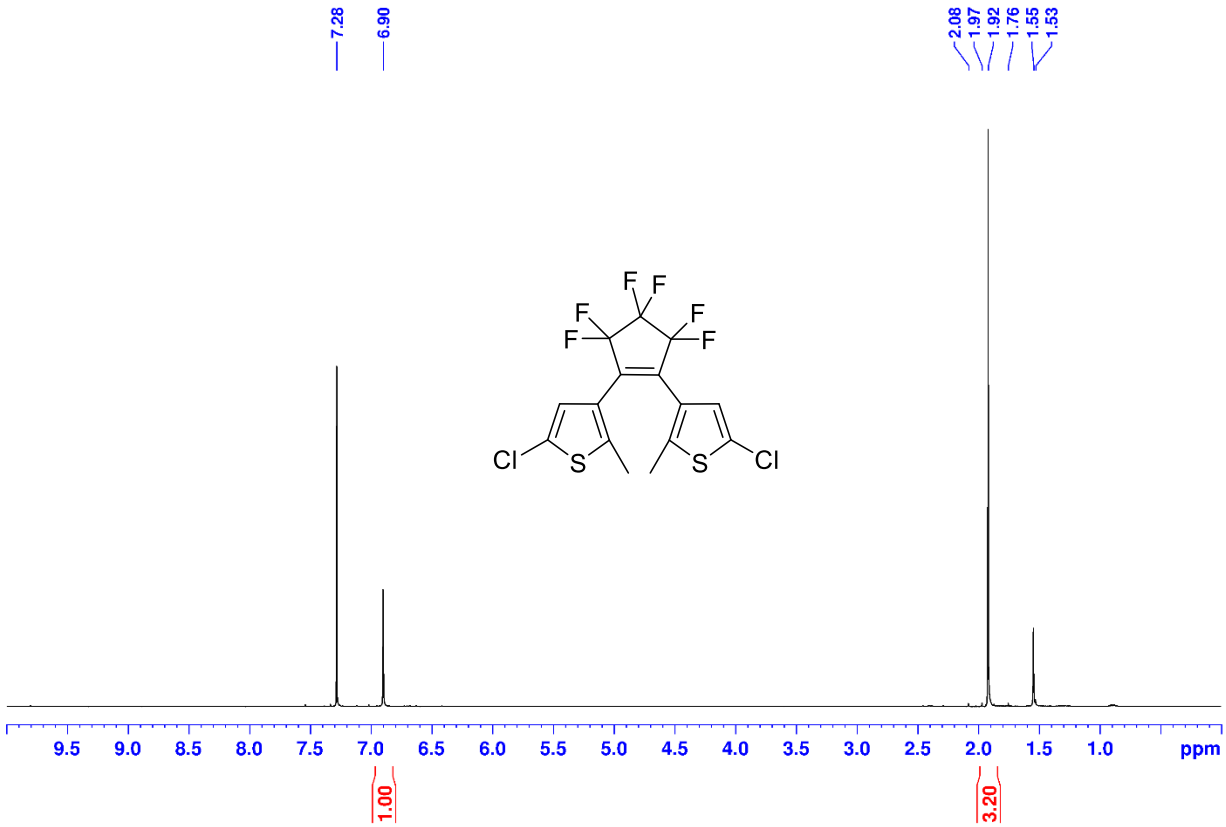
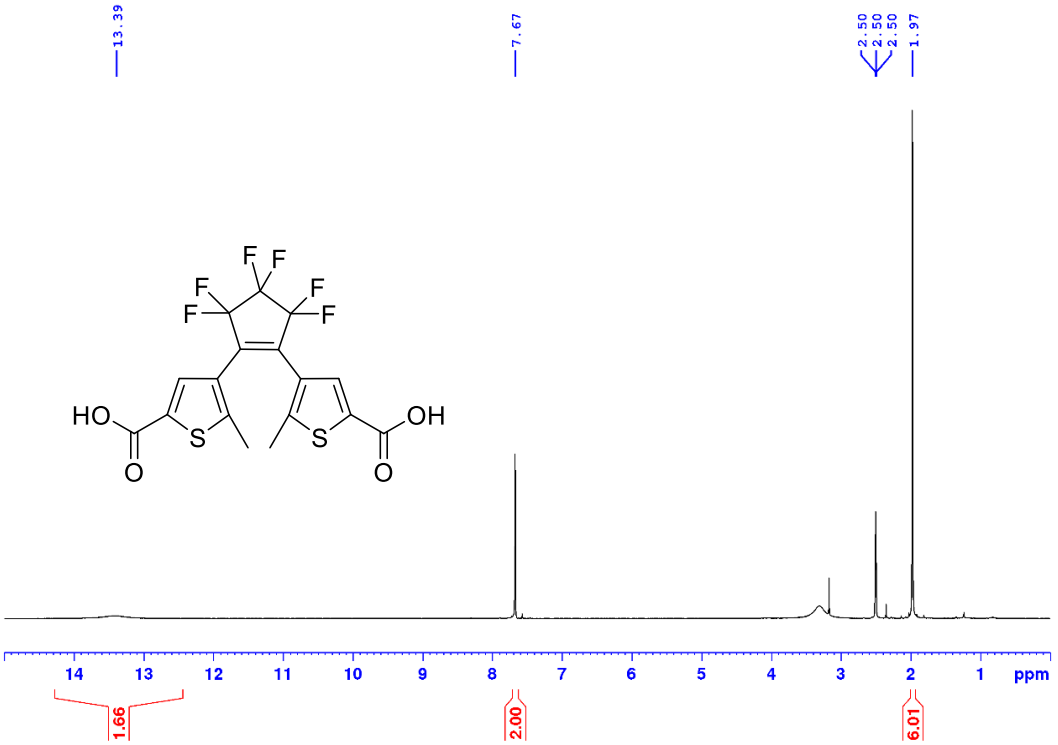


Fig. S2 ^{1}H spectra of compound **S2** in $CDCl_3$.


13.39
7.67
2.50
2.50
2.50
1.97
F
F
F
F
F
F
HO
O
S
S
OH
O
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9
8
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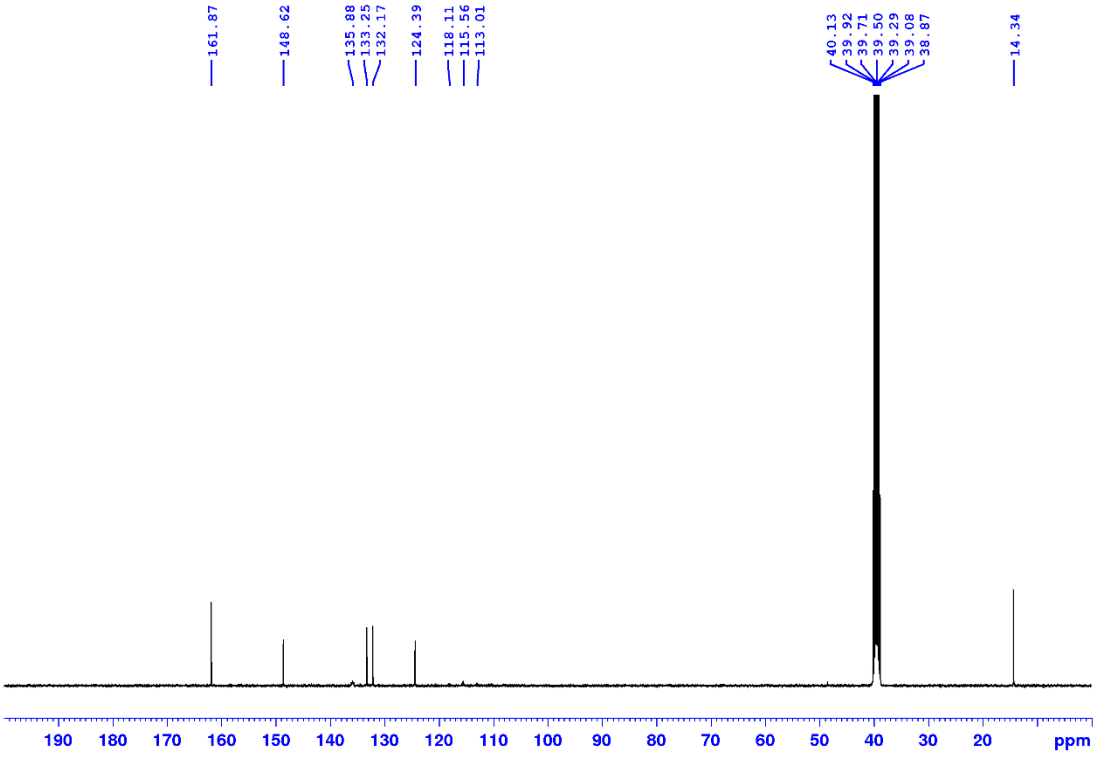
5
4
3
2
1
ppm
1.66
2.00
6.01


161.87
148.62
135.88
133.25
132.17
124.39
118.11
115.56
113.01
40.13
39.92
39.71
39.50
39.29
39.08
38.87
14.34
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110
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70
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ppm

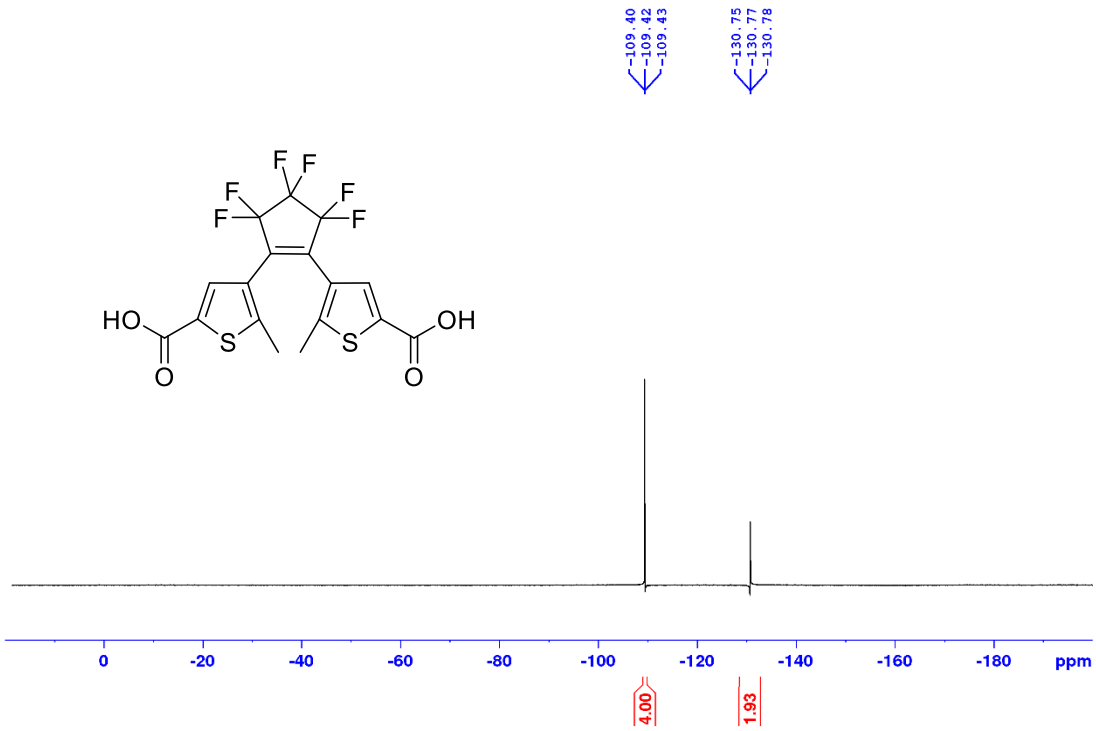

Fig. S3 ^{1}H, ^{13}C NMR, and ^{19}F NMR spectra of compound **2F** in d_6-DMSO.

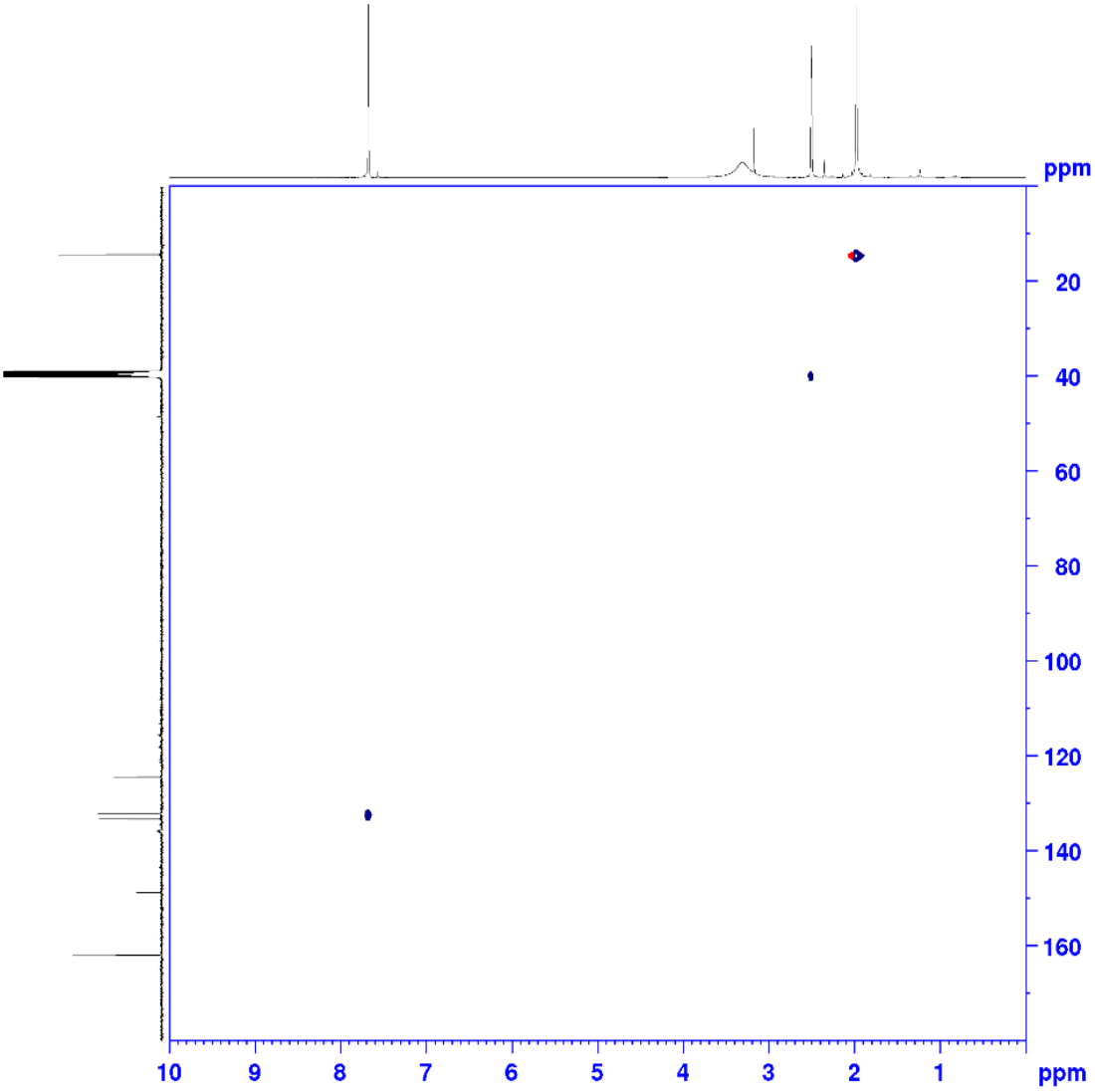

Fig. S4 HSQC NMR spectrum of compound **2F**.

Synthesized QD Absorbance and PL:

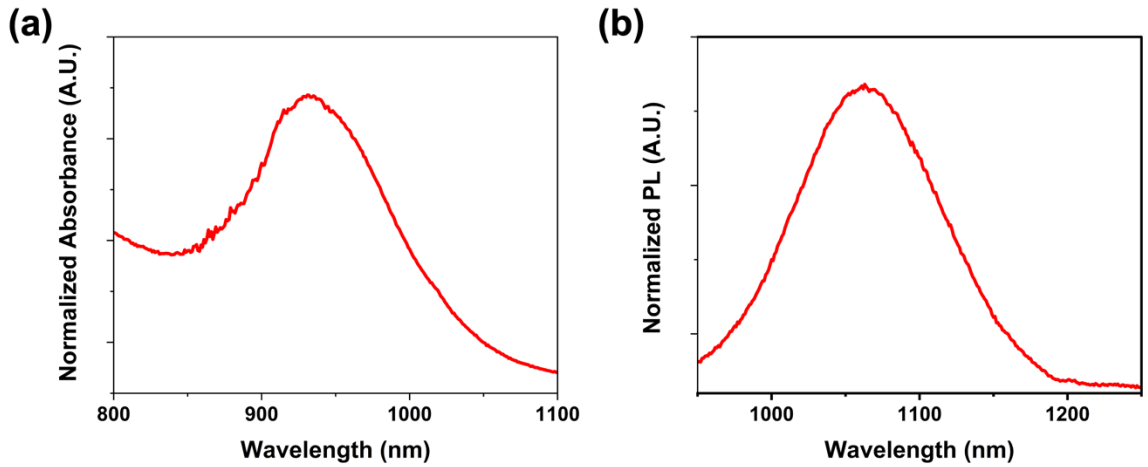

Fig. S5 Normalized (**a**) absorbance and (**b**) PL spectra of the synthesized QDs

The QD absorbance peak was measured around 940 nm which was determined to correspond to a QD diameter of ~3.2 nm using a sizing curve in literature.[4] QDs were excited with 750 nm light and PL was measured to occur around 1060 nm.

Thin Film Absorbances:

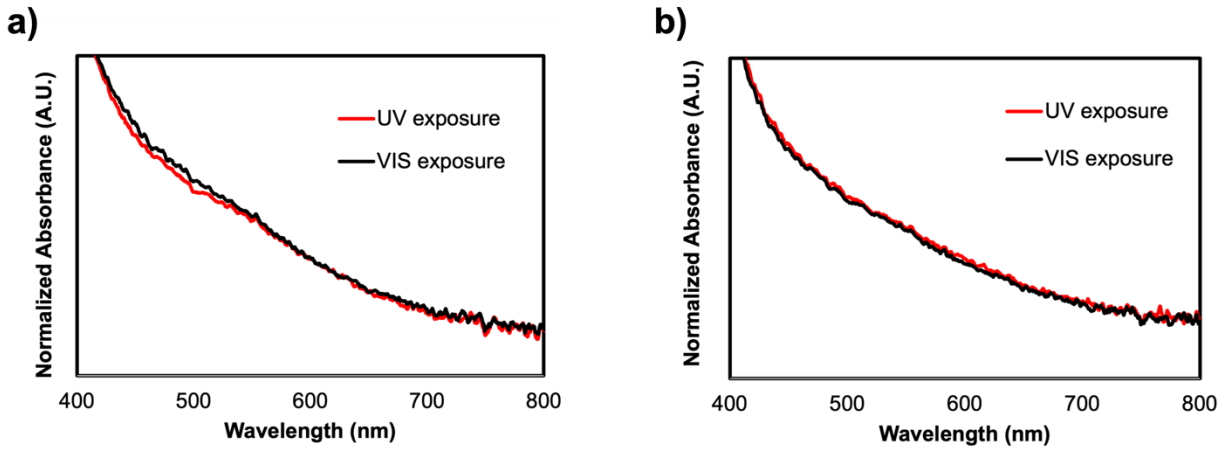

Fig. S6 Absorbances of QD thin films crosslinked with (**a**) 1H and (**b**) 2F after UV and VIS exposure. Results show that the amount of absorbance of the samples does not appreciably change with the change in molecular configuration.

Asymptotic PL Switching:

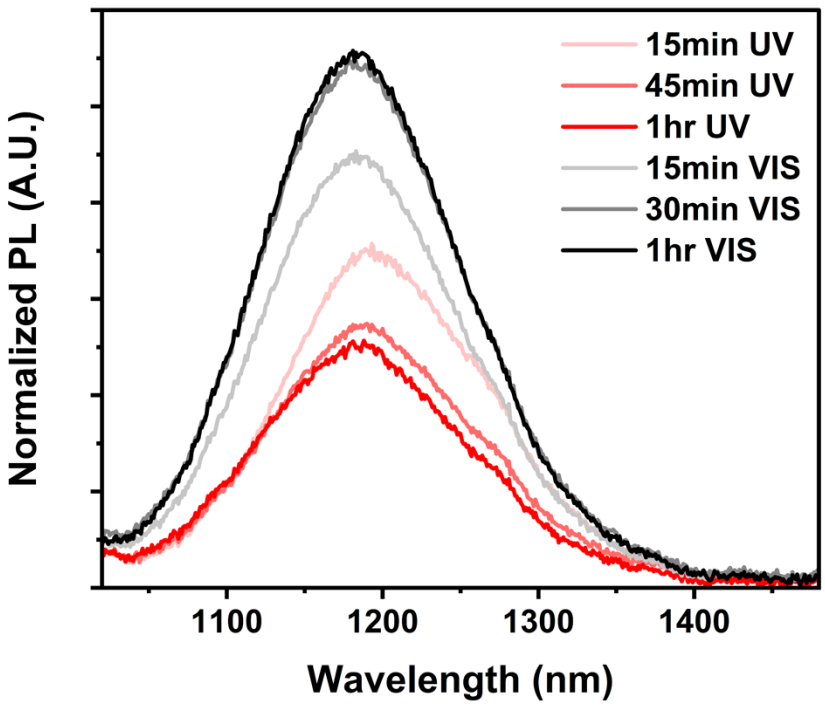

Fig. S7 PL switching as observed after increasing Visible and UV exposure time. This figure demonstrates that the sample does reach an asymptotic switching limit after increasing exposure.

Raw Data for PL measurements on the PCM treated QD samples:

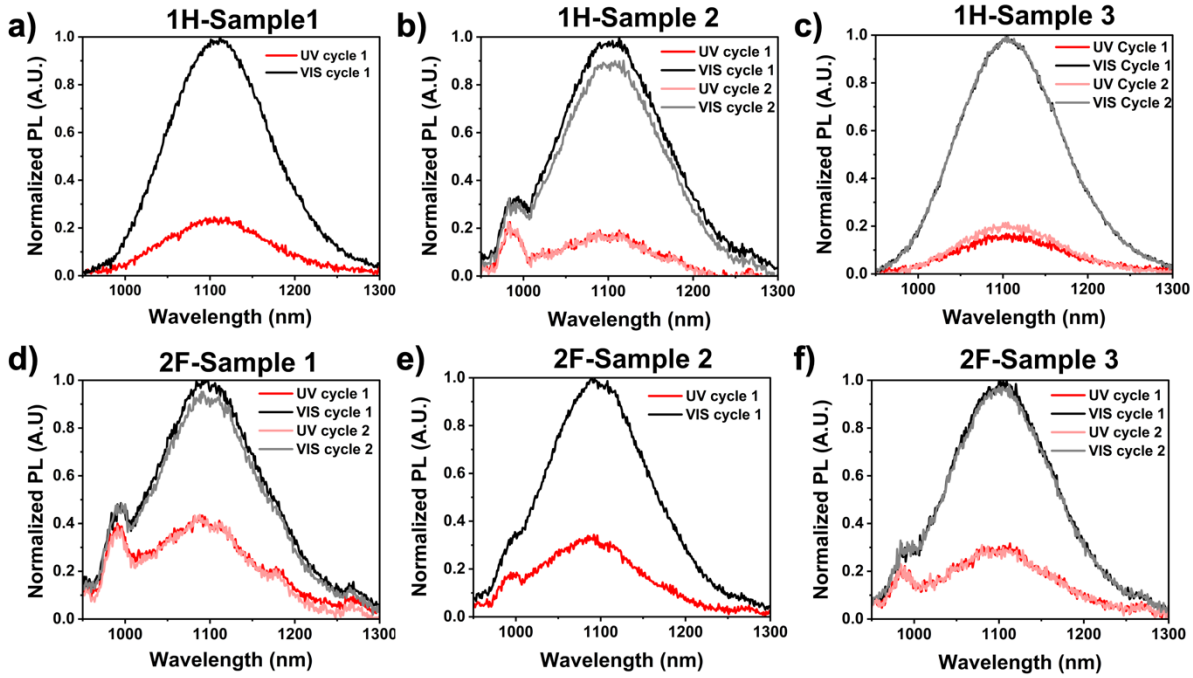

Fig. S8 PL measurement for three samples of QDs crosslinked with (**a-c**) **1H** and (**d-e**) **2F**

Lifetime Measurements:

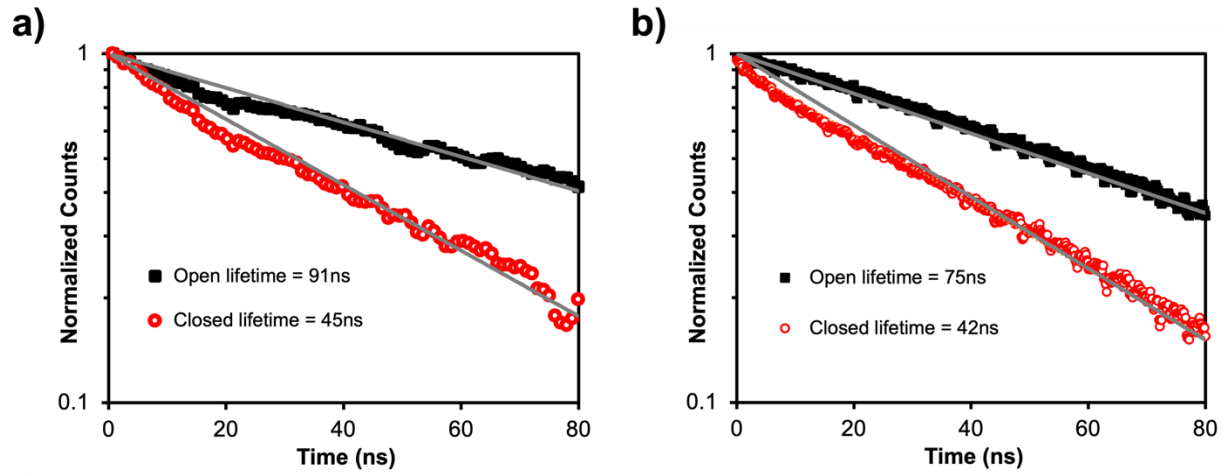

Fig. S9 Excitonic lifetime measurements for QD films crosslinked with (**a**) 1H and (**b**) 2F. Fit lines for the exponentials are shown in grey.

Absorbance mono-esterified ligand molecules:

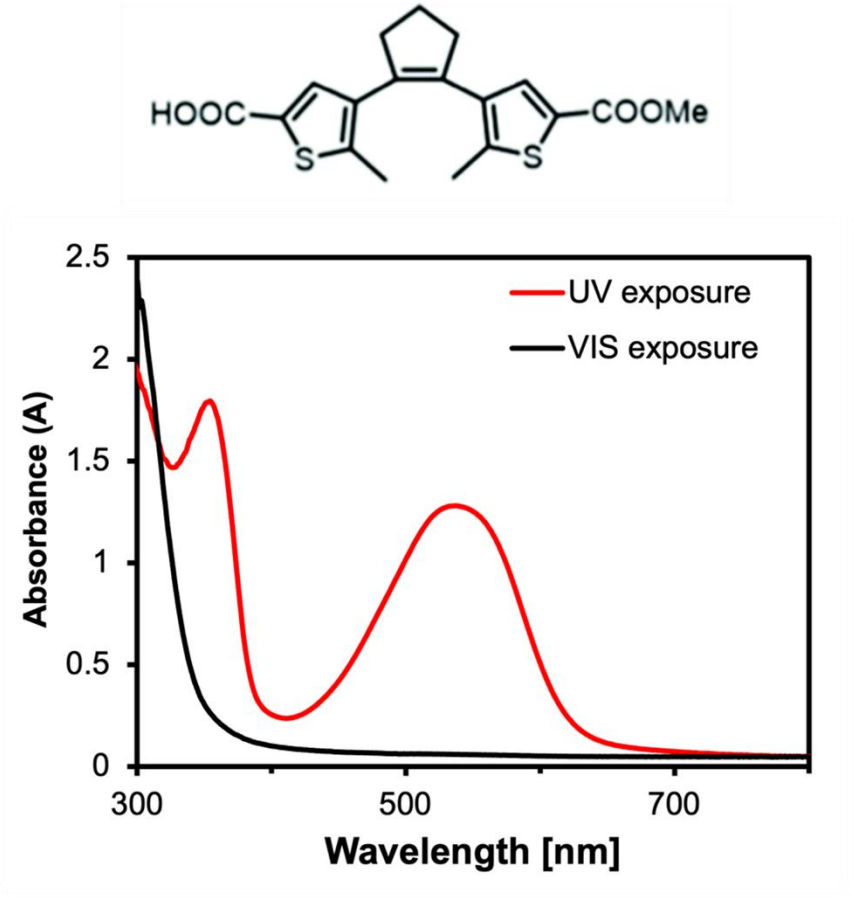

Fig. S10 The absorbance of the free mono-esterified ligand molecules in solution in its open and closed states.

PL of QD with ligand 1H and Mono-esterified PCM in Solution:

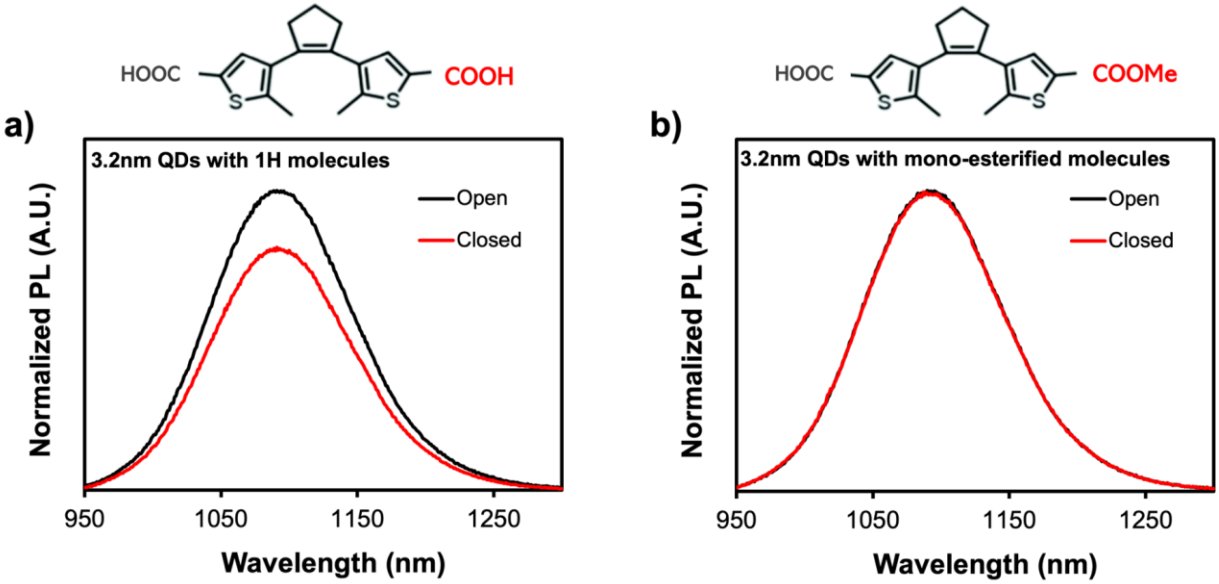

Fig. S11 PL spectra of QDs in solution with (a) molecule 1H (b) the mono-esterified ligand in their open and closed configurations. A significant PL switching effect is observed in QD solutions with addition of 1H molecules but not for the mono-esterified molecules.

GISAXS Results:

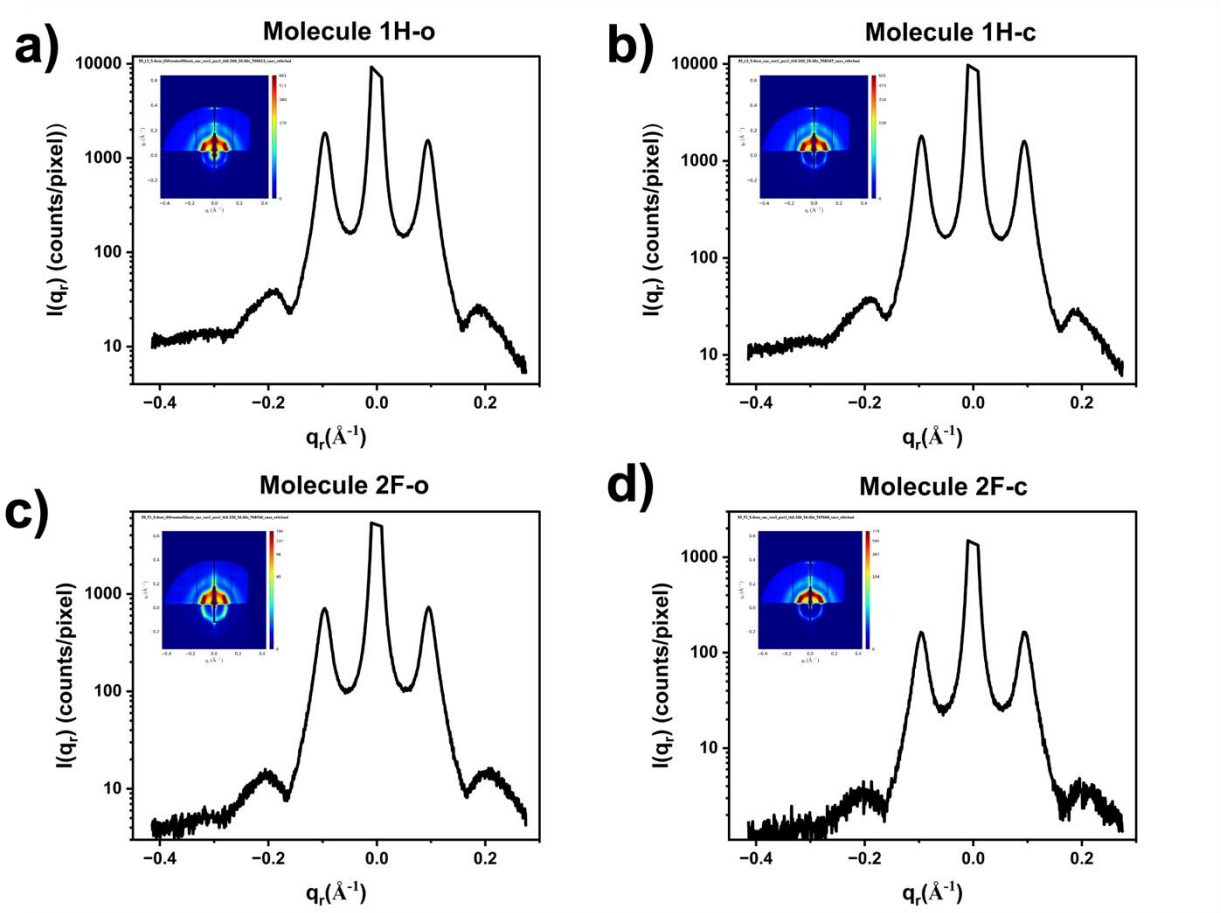

Fig. S12 GISAXS measurements of molecule **1H** in the (a) open and (b) closed configurations and of molecule **2F** in the (c) open and (d) closed configurations.

Since the quantum dots used for these measurements were 5.6 nm in diameter, these results show that edge to edge distances between quantum dots were around 1 nm in length for both **1H** and **2F** and change by <0.1 nm upon configuration change

QD size = 5.6 nm

Connecting Ligands	PCM – "Closed" state Average Inter-QD Distance	PCM – "Open" state Average Inter-QD Distance
Molecule 1H	65.9 Å	66.5 Å
Molecule 2F	65.6 Å	66.6 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˚.

Oxidation Spectra:

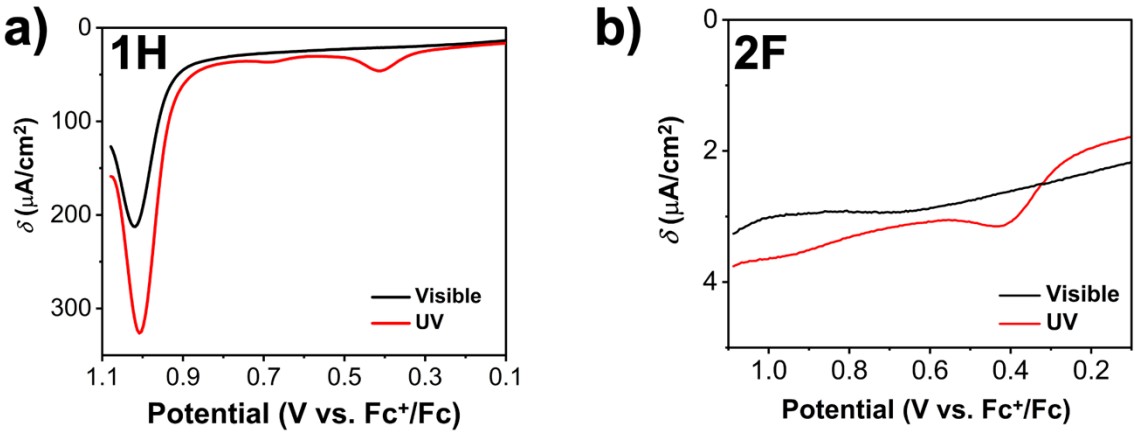

Fig. S13 DPVs at oxidizing potentials for molecules (**a**) **1H** and (**b**) **2F** respectively. **1H** results match those that have appeared previously in literature.[5]

Mathematical Background:

To better understand the behavior of our system, we must understand the fates of the QD confined excitons after NIR light illumination. These excitons can go through a host of competing relaxation mechanisms which can be classed either as radiative recombination or as nonradiative recombination (surface trapping of charges and Auger recombination). For this experiment, we effectively introduce charge tunneling between adjacent quantum dots as another mechanism for non-radiative recombination. Therefore, the rate of exciton dissociation for our particles is

$$k_{total} = k_r + k_{nr} + k_T \tag{1}$$

Where k_{total} is the total rate of exciton decay, k_r is the rate of radiative decay, k_{nr} the rate of non-radiative decay (by all pathways except for tunneling), and k_T the tunneling rate. Since we are interested in the total amount of PL, we can represent the total fraction of excitons which dissociate radiatively (N) as

$$N = \frac{\int e^{-k_{total}t}dt}{\int e^{-k_r t}dt} = \frac{k_r}{k_{total}} \tag{2}$$

After switching the state of the photochromic molecule, we only change the rate of tunneling k_T giving us, $k_{T,closed}$ for the closed state and $k_{T,open}$ for the open state. Therefore, comparing the two total PLs of the open and closed states gives the theoretical switching amount A which is defined as the integrated PL curve of the QDs in the open configuration of the PCM divided by the integrated PL curve of the QDs in the closed configuration of the PCM.

$$\mathrm{A} = \frac{k + k_{T,closed}}{k + k_{T,open}} \tag{3}$$

Where k is $k_r + k_{nr}$. Assuming that the barrier width does not significantly change after PCM switching, we use the tunneling approximation $k_T \propto e^{-\alpha\sqrt{E_{PCM}-E_{QD}}}$ where E_{PCM} is the energy of the photochromic molecule, E_{QD} is the energy level of the quantum dot, and α is a physical constant given by the expression

$$\alpha = \frac{2d\sqrt{2m}}{\hbar} \tag{4}$$

Where d is the barrier width (~1 nm for our system) and m is the effective mass of the tunneling charge. Next, assuming that the electronic coupling coefficient changes minimally upon PCM switching, we take $k_T = \beta e^{-\alpha\sqrt{E_{PCM}-E_{QD}}}$ where β is a constant. This approximation is physically justified since the end groups of **1H** and **2F** are identical. Finally, dividing through by k, we write

$$A = \frac{1 + \gamma e^{-\alpha\sqrt{E_{PCM,closed}-E_{QD}}}}{1 + \gamma e^{-\alpha\sqrt{E_{PCM,open}-E_{QD}}}} \tag{5}$$

Where $\gamma = \beta/k$. To simplify the analysis of our system we represent the energies in the following way. We define $E_{alignment} = E_{PCM,closed} - E_{QD}$ which represents the alignment of the PCM energy levels with the energy levels of the quantum dots and $E_{gap} = E_{PCM,open} - E_{PCM,closed}$ which gives the energy level change between open and closed configurations of the PCM. This allows us to rewrite equation (4) in the following way

$$A = \frac{1+\gamma e^{-\alpha\sqrt{E_{alignment}}}}{1+\gamma e^{-\alpha\sqrt{E_{gap}+E_{alignment}}}} \tag{6}$$

Equation 6 gives the general formula for the switching performance of tunneling based photo switches. Here it is interesting to consider the limiting cases of this formula. Minimum A is achieved by E_{gap} = 0 which gives the condition of no switching and in which case A = 1. The maximum possible A occurs when $E_{alignment}$ = 0 and E_{gap} is large, in which case A = 1 + γ.

DFT Energy results

	HOMO energy [eV]		LUMO energy [eV]	
	DFT	DPV	DFT	DPV
1H-open	-5.98	-6.26	-1.88	-2.14
1H-closed	-5.32	-5.25	-2.97	-2.97
2F-open	-7.05	-6.64	-2.72	-2.51
2F-closed	-6.21	-5.41	-3.93	-3.30

Table S2 Energy levels for molecules **1H** and **2F** in their open and closed configurations obtained using DFT and DPV.

References

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3. L. U. Yoon, S. B. Adhikari, E. S. Sarabamoun, J. M. Bietsch, E. H. R. Tsai, G. Wang and J. J. Choi, *Journal of Materials Chemistry C*, 2021, **9**, 16006-16013.
4. J. Jasieniak, M. Califano and S. E. Watkins, *ACS Nano*, 2011, **5**, 5888-5902.
5. G. Guirado, C. Coudret, M. Hliwa and J.-P. Launay, *The Journal of Physical Chemistry B*, 2005, **109**, 17445-17459.