

Supporting Information

Surface-Functionalized CdS Clusters with Recognition Sites near the Interface: Selective Luminescence Response to Lipophilic Phenols

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General: ^1H NMR spectra were measured in CDCl_3 on a JEOL Type ECX400 spectrometer at room temperature, and the chemical shifts were determined with respect to internal solvent signals. IR spectra were measured on a JASCO Type FTIR-400 as KBr pellets. Electronic absorption spectra were measured on a JASCO Type V-550 UV/VIS spectrophotometer by using a quartz cell with a 1-cm path length. Photoluminescence and excitation spectra were recorded on a JASCO FP-6500 spectrofluorometer equipped with a Hamamatsu Photonics R928 photomultiplier tube detector. An optical filter was applied before the detector window to remove wavelengths below 360 nm, thus avoiding the second-order effects of the excitation light.

Materials: Poly(ethyleneglycol) monomethyl ether ($\text{HO}-(\text{C}_2\text{H}_4\text{O})_m\text{-Me}$, $M_n \sim 350$) was purchased from Alfa. The averaged degree of polymerization (m) was estimated to be 7 from the integrated areas of the ^1H NMR signals due to the methylene units (δ 3.49 - 3.71) and that of the singlet signal (δ 3.34) due to the terminal methyl group. 11-Bromo-1-undecanol (>97%), 6-chloro-1-hexanol (>95%), potassium phthalimide (>98%), 4-mercaptobenzoic acid (>98%), 1-ethyl-3-(dimethylaminopropyl)carbodiimide (EDC) (>97%), 1-hydroxybenzotriazole monohydrate (HOBt· H_2O) (>97%), 3,3'-dithiodipropionic acid (>99%), bisphenol A (>99%), 1-undecanol (>98%), and thiophenol (>98%) were obtained from TCI. 4-Nonylphenol (>97%) was obtained from Kanto Chemical. 8-Chloro-1-octanol (98%) and 11-bromo-1-undecene (95%) were purchased from Aldrich. Phenol (>99%), resorcinol (>99%), hydroquinone (>99%), and cadmium nitrate tetrahydrate were obtained from Wako Chemical. Tricine (>99%) was purchased from Dojindo. Other standard chemicals and solvents were obtained from Wako Chemical or Kanto Chemical. The reagents and solvents were used as received without further purification. ' $\text{Cd}_{10}\text{S}_{16}\text{Ph}_{12}$ ' was synthesized in three steps from cadmium nitrate tetrahydrate and thiophenol according to the literatures.¹ 4,4'-Dithiodibenzoic acid was synthesized by iodine oxidation of

4-mercaptobenzoic acid.

Synthesis of PEG-appended thiols (Scheme S1). PEG-appended amines (**4**, **6-C6**, **6-C8**, and **6-C11**) were synthesized in similar manners to those reported in the literature.²

4,4'-dithiodibenzamides (**5**, **7-C6**, **7-C8**, **7-C11**) were prepared from 4,4'-dithiodibenzoic acid and the corresponding amine utilizing the acid chloride method (SOCl₂ / DMF).

3,3'-dithiopropioamide (**8**) was prepared by the standard EDC/HOBt-mediated coupling of 3,3'-dithiodipropionic acid with **5-C8**.

5: ¹H NMR (CDCl₃): δ 7.76 (d, 2H, Ar-H), 7.55 (d, 2H, Ar-H), 6.83 (br, 1H, NH), 3.85 - 3.60 (m, 28H, PEG), 3.55 (t, 2H, CH₂-OPEG), 3.36 (s, 3H, OCH₃).

7-C6: ¹H NMR (CDCl₃): δ 7.70 (d, 2H, Ar-H), 7.45 (d, 2H, Ar-H), 6.18 (br, 1H, NH), 3.65 - 3.54 (m, 28H, PEG), 3.41 (t, 2H, CH₂-OPEG), 3.35 (s, 3H, OCH₃), 1.56 (m, 4H, CH₂-CH₂-OPEG and CH₂-CH₂-N), 1.36 (br, 4H, aliphatic CH₂).

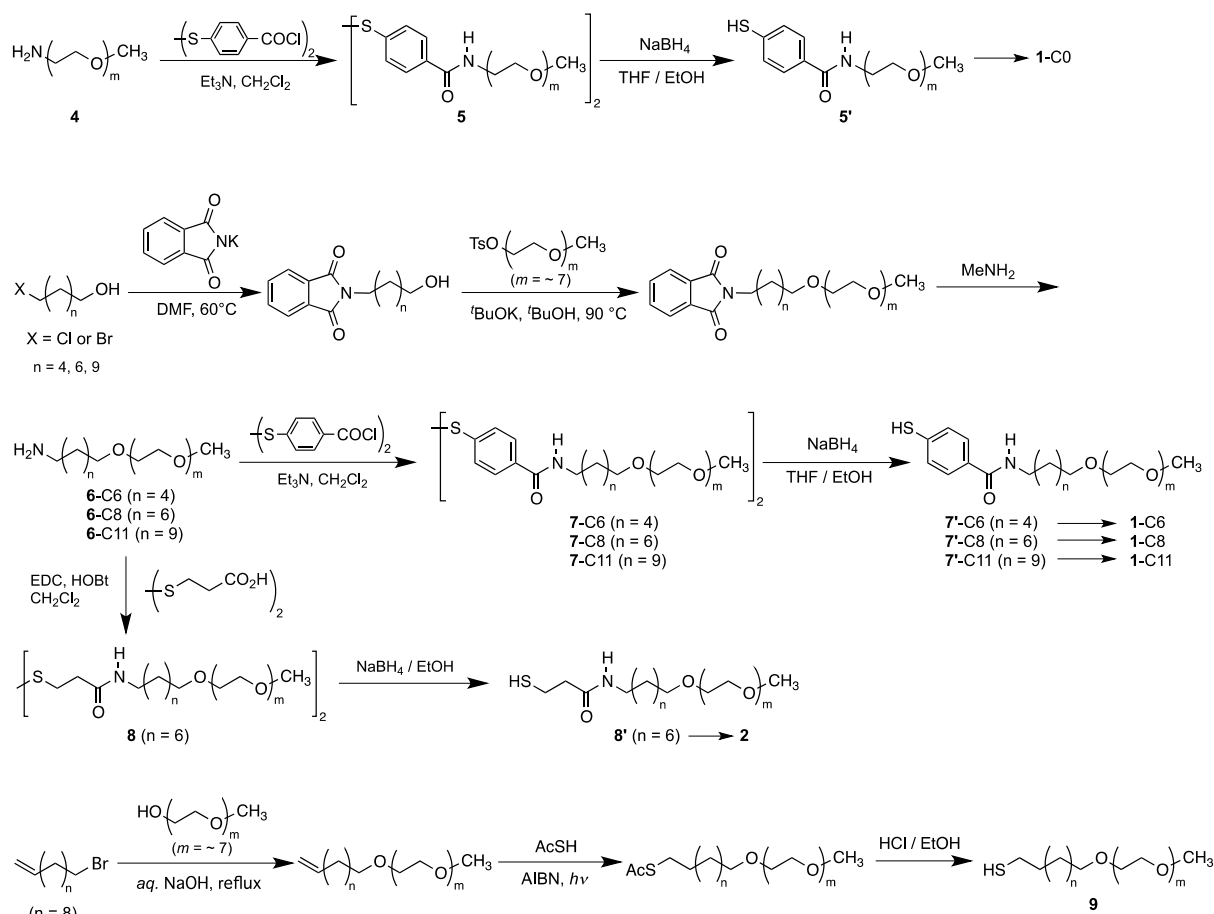
7-C8: ¹H NMR (CDCl₃): δ 7.69 (d, 2H, Ar-H), 7.48 (d, 2H, Ar-H), 6.14 (br, 1H, NH), 3.68 - 3.53 (m, 28H, PEG), 3.41 (t, 2H, CH₂-OPEG), 3.33 (s, 3H, OCH₃), 1.56 (m, 4H, CH₂-CH₂-OPEG and CH₂-CH₂-N), 1.27 (br, 8H, aliphatic CH₂).

7-C11: ¹H NMR (CDCl₃): δ 7.77 (d, 2H, Ar-H), 7.45 (d, 2H, Ar-H), 6.09 (br, 1H, NH), 3.68 - 3.35 (m, 28H, PEG), 3.40 (t, 2H, CH₂-OPEG), 3.33 (s, 3H, OCH₃), 1.58 (m, 4H, CH₂-CH₂-OPEG and CH₂-CH₂-N), 1.28 (br 14H, aliphatic CH₂).

8: ¹H NMR (CDCl₃): δ 6.00 (s, 1H, N-H), 3.63 - 3.53 (m, 28H, PEG), 3.42 (t, 2H, CH₂-OPEG), 3.37 (s, 3H, O-CH₃), 3.22 (m, 2H, N-CH₂), 2.95 (m, 2H, S-CH₂), 2.54 (m, 2H, CH₂-CO), 1.60 - 1.40 (br, 4H, CH₂-CH₂-OPEG and CH₂-CH₂-N), 1.26 (br, 12H, aliphatic CH₂).

Disulfides (**5**, **7**, **8**) thus obtained were converted into thiols (**5'**, **7'**, **8'**) by conventional NaBH₄ reduction method. The corresponding disulfide (1.46 mmol) and NaBH₄ (14.6 mmol) were mixed in a THF/EtOH mixture (15 mL each) at 0 °C, and the resulting solution was stirred at room temperature for 6 h. Usual work-up procedure (quenching with aq. HCl, then extraction with dichloromethane) afforded an oily residue containing the desired product, which was directly used for the subsequent ligand exchange reaction.

ω-PEGylated-1-undecanethiol (**9**) having no amide linkages was prepared from 11-bromo-1-undecene according to literatures.³



Scheme S1. Synthesis of precursor thiols.

General synthesis of functionalized clusters: Thiol (2.0 mmol) was added to a suspension of 'Cd₁₀S₁₆Ph₁₂' (74 mg, 0.029 mmol) in dry MeCN (8 mL), and the mixture was heated at 60 °C. As the progress of the reaction, the mixture became homogeneous. After 24 h, the solvents were removed by evaporation and the residue was sonicated with ether and the supernatant was discarded. The same procedure was repeated three times to ensure the complete removal of free thiols. The oily residue thus obtained was freeze-dried from benzene to give a hygroscopic pale yellow tan solid. The extent of the ligand exchange reaction was assessed by IR spectra and elemental analyses of the isolated product.

1-C0: calcd (%) for Cd₁₀S₄(SC₆H₄CONH(C₂H₄O)₇CH₃)₁₂(H₂O)₁₂: C 44.26, H 6.41, N 2.35, S 7.16; found: C 44.12, H, 6.31, N, 2.32, S, 7.11.

1-C6: calcd (%) for Cd₁₀S₄(SC₆H₄CONH(CH₂)₆O(C₂H₄O)₇CH₃)₁₂(H₂O)₁₀: C 48.45, H 7.21, N 2.02, S 6.16; found: C 48.35, H, 7.30, N, 2.26, S, 6.02.

1-C8: calcd (%) for Cd₁₀S₄(SC₆H₄CONH(CH₂)₈O(C₂H₄O)₇CH₃)₁₂(H₂O)₅: C 50.41, H 7.45, N 1.96, S 5.98; found: C 50.43, H, 7.55, N, 2.25, S, 6.20.

1-C11: calcd (%) for Cd₁₀S₄(SC₆H₄CONH(CH₂)₁₁O(C₂H₄O)₇CH₃)₁₂(H₂O)₁₀: C 51.86, H 7.87,

N 1.83, S 5.59; found: C 51.63, H, 7.74, N, 2.11, S, 5.59.

The propioamide-type thiol (**8'**) appeared reluctant to undergo the ligand exchange reaction.

The ^1H NMR spectrum and elemental analyses of the cluster after the ligand exchange reaction (**2**) showed that some S-phenyl groups remained intact.

calcd (%) for $\text{Cd}_{10}\text{S}_4(\text{SC}_2\text{H}_4\text{CONH}(\text{CH}_2)_8\text{O}(\text{CH}_2\text{CH}_2\text{O})_7\text{CH}_3)_{11.5}(\text{SPh})_{0.5}(\text{H}_2\text{O})_5$: C 46.64, H 7.91, N 2.07, S 6.59; found: C 46.54, H 7.71, N 1.81, S 6.31.

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- 1 I. G. Dance, A. Choy, M. L. Scudder, *J. Am. Chem. Soc.* **1984**, *106*, 6285; W. E. Farneth, N. Herron, Y. Wang, *Chem. Mater.* **1992**, *4*, 916.
 - 2 E. Obert, M. Bellot, L. Bouteiller, F. Andrioletti, C. Lehen-Ferrenbach, F. Boué, *J. Am. Chem. Soc.* **2007**, *129*, 15601.
 - 3 Pale-Grosdemange, C.; Ethan, C.; Simon, S.; Prime, K. L.; Whitesides, G. M. *J. Am. Chem. Soc.* **1991**, *113*, 12; Houseman, B. T.; Mrksich, M. *J. Org. Chem.* **1998**, *63*, 7552.

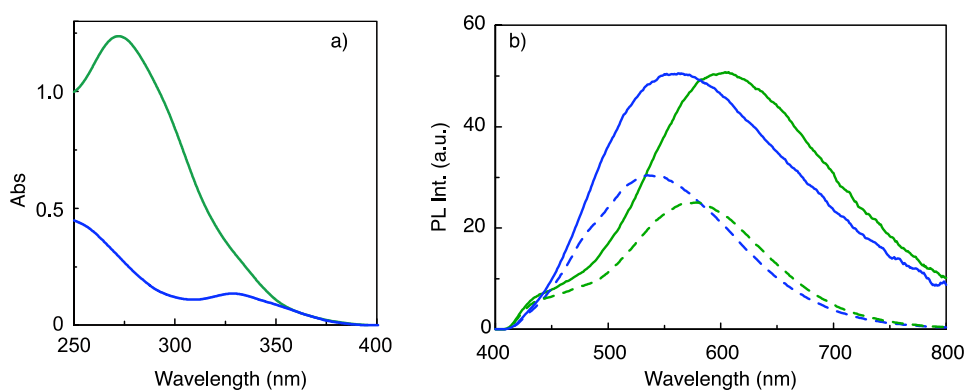


Figure S1. a) Absorption, b) uncorrected PL (dashed) and corrected PL (solid) spectra of **1**-C8 (green) and **2** (blue) in 10-mM tricine buffer.

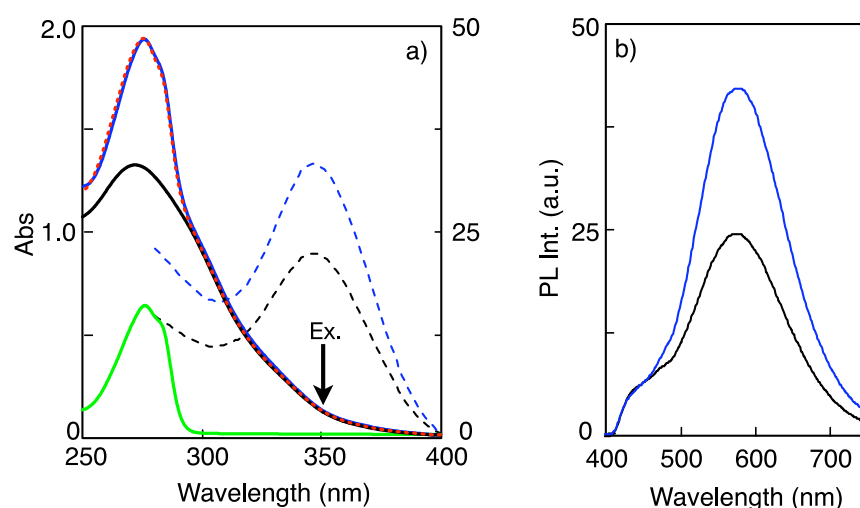


Figure S2. a) Absorption (solid lines) and PL excitation ($\lambda_{\text{em}} = 590$ nm, uncorrected) (dashed lines) spectra, and b) PL emission spectra ($\lambda_{\text{ex}} = 350$ nm, uncorrected) of **1**-C8 before (black) and after the addition of BPA ($[\text{BPA}] = 0.20$ mM) (blue) in 10-mM tricine buffer at 25 °C. The absorption spectrum of BPA alone (0.20 mM) (green) and the sum of the spectra of **1**-C8 and BPA (red dotted) are also shown. The spectrum of **1**-C8 in the presence of BPA (blue solid) is almost identical to the sum spectrum (red).

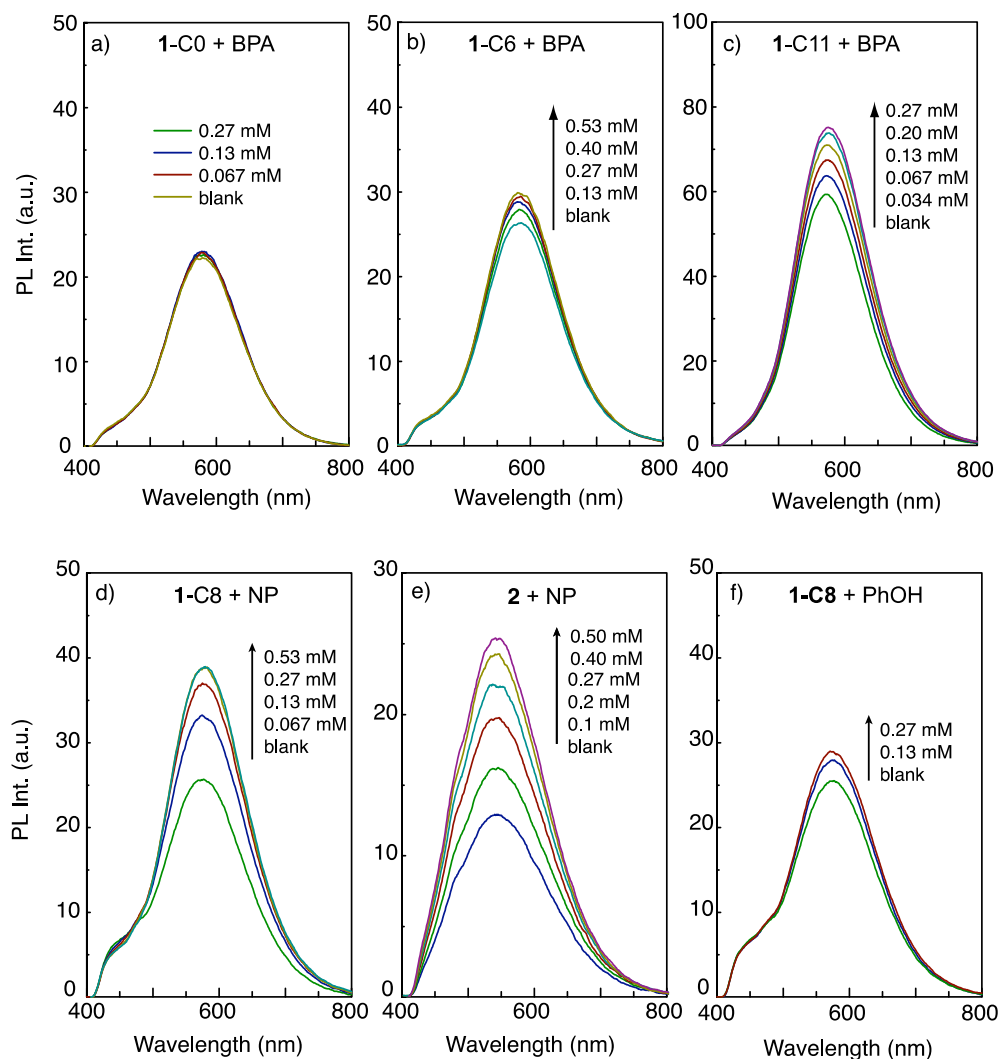


Figure S3. Photoluminescence titration with BPA, NP, and phenol.

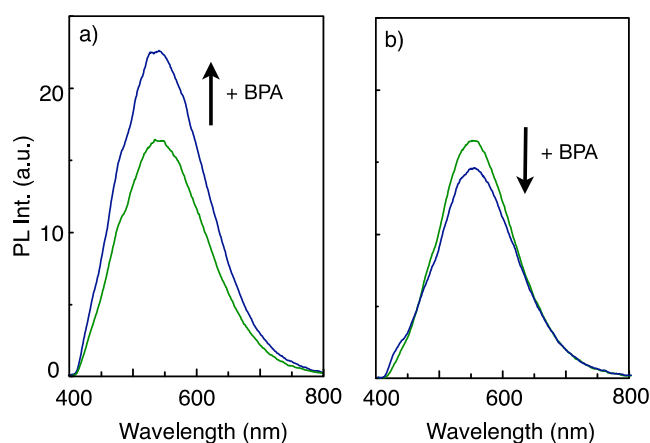


Figure S4. Photoluminescence responses of a) 2 and b) 3 (right) in 6% MeCN / water before (green) and after (blue) the addition of BPA ([BPA] = 0.4 mM).

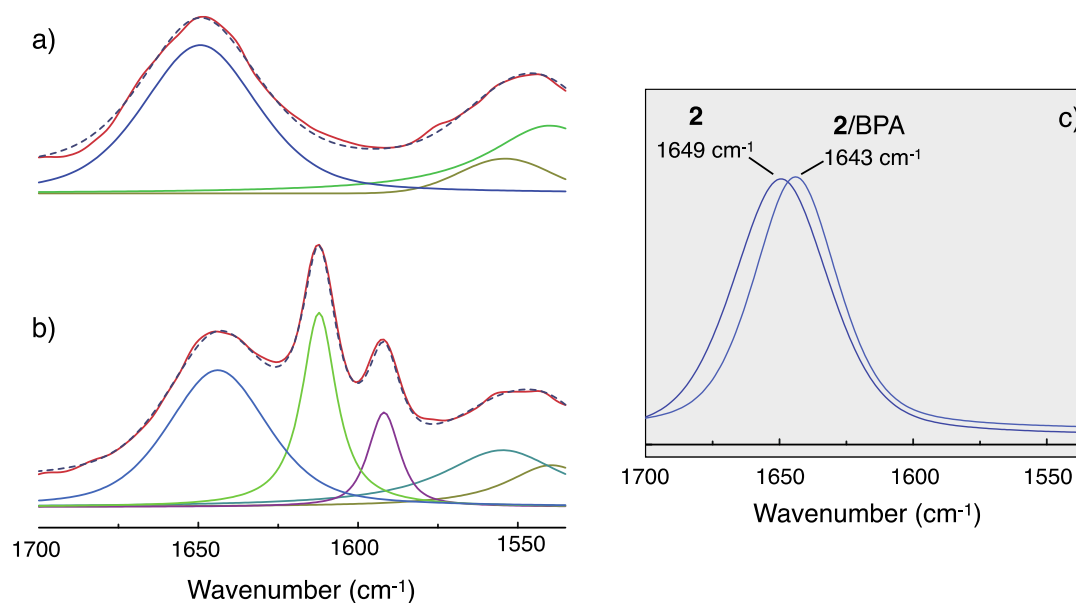


Figure S5. Separation of the overlapped bands of the spectra of a) **2** (Figure 5a) and b) **2/BPA** (Figure 5b) by the combination of Gaussian and Lorentz curves using a curve-fitting software equipped with JASCO FTIR-400 spectrometer. Red lines indicate the raw spectra and dashed lines indicate the sums of the separated bands. Separated amide I bands of **2** and **2/BPA** are superimposed for comparison (c).

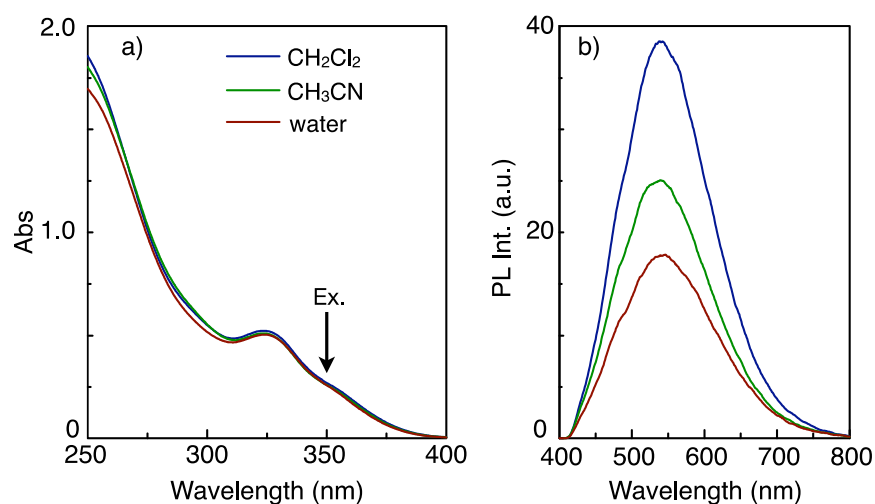


Figure S6. a) UV-visible and b) photoluminescence ($\lambda_{\text{ex}} = 350$ nm, uncorrected) spectra of **1** in dichloromethane (blue), acetonitrile (green), and Milli-Q water (red).