SUPPORTING INFORMATION

Unexpected electronic perturbation effects of simple PEG environments on the optical properties of small cadmium chalcogenide clusters

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Syntheses of PEGylated thiols

Thiol-terminated PEGs (HS-PEGn) for **1**-PEGn were prepared from tri(ethylene glycol) monomethyl ether (n = 3) and poly(ethylene glycol) monomethyl ethers (n = ~7, ~17 and ~46 for M_w = 350, 750 and 2000, respectively). HS-$(CH_2)_m$-CONH-PEG17 for **2**-C_m-PEG17 (m = 2, 3, 7, 10) were prepared from amino-terminated poly(ethylene glycol) monomethyl ethers with M_w of 750. HS-$(CH_2)_{11}$-$(OCH_2CH_2)_n$OCH$_3$ (n = ~17) for **3** was prepared according to a literature method reported for analogous compounds (N. Bonnet, D. O'Hagan and G. Hähner, *Chem. Commun.*, 2007, **47**, 5066-5068). The outline of the synthetic routes is shown in Schemes S1.

TsO$(CH_2CH_2O)_3$CH$_3$ (**TsO-PEG3**): To a mixture of *p*-toluenesulfonyl chloride (34.9 g, 183.1 mmol) and triethylamine (46.1 ml, 304.9 mmol) dissolved in dichloromethane (50 ml) was added slowly tri(ethylene glycol) monomethyl ether (10.0 g, 60.9 mmol) at 0 ℃, and the resultant solution was stirred at room temperature under N$_2$ for 24 h. Aq. HCl (1.0 M) was added to the reaction mixture and the separated organic layer was successively washed with aq. NaHCO$_3$ and then with water, dried over MgSO$_4$, and filtered. The filtrate was evaporated and the residue was subjected to silica gel column chromatography (Silica Gel 60 N; Kanto Chemical) with dichloromethane / methanol (20 / 1 v/v) as eluent to give TsO-PEG3 as yellow oil (33.6 g, 94 %). ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.80 (d, 2H, Ar-H), 7.32 (d, 2H, Ar-H), 4.16 (t, 2H, -CH$_2$-O-Ts), 3.90-3.40 (m, 10H, O-CH$_2$-CH$_2$-O). 3.36 (s, 3H, O-CH$_3$), 2.45 (s, 3H, Ar-CH$_3$).

TsO$(CH_2CH_2O)_n$CH$_3$ (n = ~7 (**TsO-PEG7**), n = ~17 (**TsO-PEG17**), n = ~46 (**TsO-PEG46**)) were prepared in similar manners to that described for the synthesis of TsO-PEG3.

TsO-PEG7: ^{1}H NMR: δ 7.80 (d, 2H, Ar-H), 7.33 (d, 2H, Ar-H), 4.15 (t, 2H, -CH$_2$-O-Ts), 3.90-3.40 (m, 26H, O-CH$_2$-CH$_2$-O). 3.37 (s, 3H, O-CH$_3$), 2.44 (s, 3H, Ar-CH$_3$).

TsO-PEG17: ^{1}H NMR: δ 7.79 (d, 2H, Ar-H), 7.33 (d, 2H, Ar-H), 4.14 (t, 2H, -CH$_2$-O-Ts), 3.90-3.40 (m, 66H, O-CH$_2$-CH$_2$-O). 3.37 (s, 3H, O-CH$_3$), 2.44 (s, 3H, Ar-CH$_3$).

TsO-PEG46: ^{1}H NMR: δ7.80 (d, 2H, Ar-H), 7.34 (d, 2H, Ar-H), 4.15 (t, 2H, -CH$_2$-O-Ts), 3.90-3.40 (m, 182H, O-CH$_2$-CH$_2$-O). 3.37 (s, 3H, O-CH$_3$), 2.45 (s, 3H, Ar-CH$_3$).

HS-$(CH_2CH_2O)_3$CH$_3$ (**HS-PEG3**): To a solution of TsO-PEG3 (4.20 g, 13.1 mmol) in ethanol (30 ml) was added thiourea (1.31 g, 17.2 mmol), and the resultant solution was refluxed under N$_2$ for 18 h. After cooled to room temperature, the reaction mixture was mixed with sodium hydroxide (0.94 g, 23.6 mmol), and then was refluxed again under N$_2$ for 5 h. After the removal of the solvents in vacuo, the residue was treated with aq. HCl (1.0 M) and the pH was adjusted

2~3. The resultant suspension was extracted with dichloromethane, and the organic layer was separated, dried over Na_2SO_4, and filtered. Evaporation of the filtrate gave **HS-PEG3** as transparent oil (2.09 g, 97 %). ^{1}H NMR: δ 3.90-3.40 (m, 10H, $O-CH_2-CH_2-O$), 3.38 (s, 3H, O-CH_3), 2.70 (q, 2H, S-CH_2).

$HS(CH_2CH_2O)_nCH_3$ (n = ~7 (**HS-PEG7**), n = ~17 (**HS-PEG17**), n = ~17 (**HS-PEG46**)) were prepared in similar manners to that described for the synthesis of **HS-PEG3**.

HS-PEG7: ^{1}H NMR: δ 3.90-3.40 (m, 26H, $O-CH_2-CH_2-O$), 3.38 (s, 3H, O-CH_3), 2.73 (q, 2H, S-CH_2).

HS-PEG17: ^{1}H NMR: δ 3.90-3.40 (m, 66H, $O-CH_2-CH_2-O$), 3.38 (s, 3H, O-CH_3), 2.70 (q, 2H, S-CH_2).

HS-PEG46: ^{1}H NMR: δ 3.90-3.40 (m, 184H, $O-CH_2-CH_2-O$), 3.38 (s, 3H, O-CH_3), 2.70 (q, 2H, S-CH_2).

$PhthN(CH_2CH_2O)_nCH_3$ (n = ~17, **PhthN-PEG17**). Potassium phthalimide (3.28 g, 17.7 mmol) and **TsO-PEG17** (13.8 g, 14.8 mmol) were dissolved in DMF (50 ml) and the solution was stirred at 60 ºC under N_2. After 24 h, the reaction mixture was treated with water / dichloromethane, and the organic layer separated was washed twice with water, dried over $MgSO_4$ and filtered. The residue after evaporation was subjected to silica gel column chromatography with dichloromethane / methanol (10 / 1 v/v) as eluent to give PhthN-PEG17 as yellow oil (12.5 g, 93 %). ^{1}H NMR: *δ* 7.84 (d, 2H, Ar-H), 7.73 (d, 2H, Ar-H), 3.90-3.40 (m, 68H, $O-CH_2-CH_2-O$). 3.37 (s, 3H, O-CH_3).

$H_2N(CH_2CH_2O)_nCH_3$ (n = ~17, **H$_2$N-PEG17**): **PhthN-PEG17** (12.5 g, 13.7 mmol) was mixed with 40% aqueous methylamine (60.0 ml, 549.4 mmol) and the mixture was stirred at room temperature. After 24 h, water and dichloromethane were added to the reaction mixture. To the organic layer separated was added aq. HCl (1.0 M) until the pH of the aqueous layer reached to 2 – 3. The aqueous layer was treated with aq. NaOH (1.0 M) until the pH reached 12 – 14. The resulting alkaline solution was extracted with dichloromethane and the organic layer was collected. After drying over Na_2SO_4 and filtration, the filtrate was evaporated to give **H$_2$N-PEG17** as transparent oil (7.27 g, 68 %). ^{1}H NMR): *δ* 3.90-3.40 (m, 66H, $O-CH_2-CH_2-O$), 3.38 (s, 3H, O-CH_3), 2.86 (t, 2H, N-CH_2).

$HS(CH_2)_2CONH(CH_2CH_2O)_nCH_3$ (n = ~17, **HS-C2-PEG17**): To a dichloromethane solution (30 mL) containing 3,3-dithiodipropionic acid (0.14 g, 0.64 mmol), 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride (0.37 g, 1.93 mmol) and 1-hydroxybenzotriazole (0.04 g, 0.26 mmol) was added **H$_2$N-PEG17** (1.50 g, 1.92 mmol) at 0 ºC, and the mixture was stirred at room temperature under N_2. After 24 h, the reaction mixture was treated with aq. HCl (1.0 M) and the separated organic layer was washed with aq. $NaHCO_3$ then with water, dried over $MgSO_4$, and filtrated. The filtrate was evaporated and the residue was subjected to silica gel column chromatography with dichloromethane / methanol (10 / 1 v/v) as eluent. The final fraction gave disulfide ($S(CH_2)_2CONH-PEG17)_2$ as transparent oil (1.03 g, 93 %), which was used in the next reaction without further purification. The disulfide thus obtained was dissolved in THF / EtOH (15 mL each) and to this solution $NaBH_4$ (1.18 g, 29.5 mol) was slowly added. After the resultant solution was stirred at room temperature for 6 h, the solvents were removed in vacuo, and the residue was treated with aq. HCl (1.0 M) to have pH of 2~3. The resultant suspension was extracted with dichloromethane, and then the organic layer was separated. After drying over Na_2SO_4 and filtration, the organic layer was evaporated to give **HS-C2-PEG17** as transparent oil (0.95 g, 93 %). ^{1}H NMR: *δ* 6.56 (s, 1H, N-H), 3.90-3.40 (m, 68H, $O-CH_2-CH_2-O$), 3.38 (s, 3H, O-CH_3), 2.81 (q, 2H, S-CH_2), 2.51 (t, 2H, CH_2-CO).

HS(CH$_2$)$_3$CONH(CH$_2$CH$_2$O)$_n$CH$_3$ (n = ~17, **HS-C3-PEG17**) was prepared in a similar manner to that described for the synthesis of **HS-C2-PEG17**. ^{1}H NMR: δ 6.28 (s, 1H, N-H), 3.90-3.40 (m, 68H, O-CH$_2$-CH$_2$-O), 3.37 (s, 3H, O-CH$_3$), 2.58 (q, 2H, S-CH$_2$), 2.32 (t, 2H, CH$_2$-CO), 1.94 (q, 2H, C-CH$_2$-C).

HS(CH$_2$)$_7$CONH(CH$_2$CH$_2$O)$_n$CH$_3$ (n = ~17, **HS-C7-PEG17**) and
HS(CH$_2$)$_{10}$CONH(CH$_2$CH$_2$O)$_n$CH$_3$ (n = ~17, **HS-C10-PEG17**) were prepared by the condensation of H$_2$N-PEG17 with 8-mercaptooctanoic acid and 11-mercaptoundecanoic acid, respectively, in similar manners to that described for the synthesis of **HS-C2-PEG17**.

HS-C7-PEG17: ^{1}H NMR: δ 6.07 (s, 1H, N-H), 3.90-3.40 (m, 68H, O-CH$_2$-CH$_2$-O), 3.38 (s, 3H, O-CH$_3$), 2.51 (q, 2H, S-CH$_2$), 2.17 (t, 2H, CH$_2$-CO), 1.80-1.20 (m, 10H, C-CH$_2$-C).

HS-C10-PEG17: ^{1}H NMR: δ 6.26 (s, 1H, N-H), 3.90-3.40 (m, 68H, O-CH$_2$-CH$_2$-O), 3.38 (s, 3H, O-CH$_3$), 2.52 (q, 2H, S-CH$_2$), 2.17 (t, 2H, CH$_2$-CO), 1.90-1.20 (m, 16H, C-CH$_2$-C).
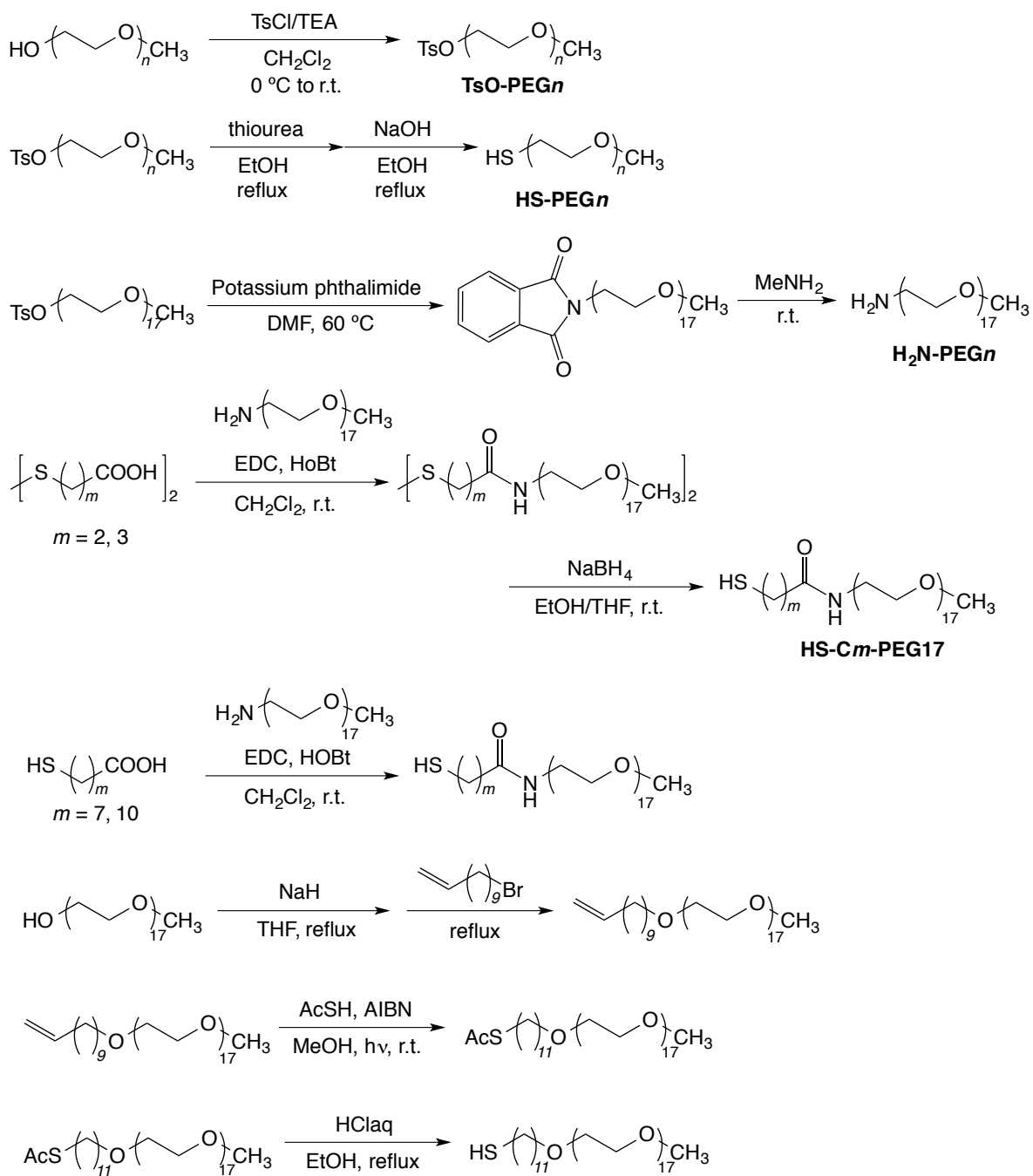
Scheme S1. Syntheses of PEGylated thiols.
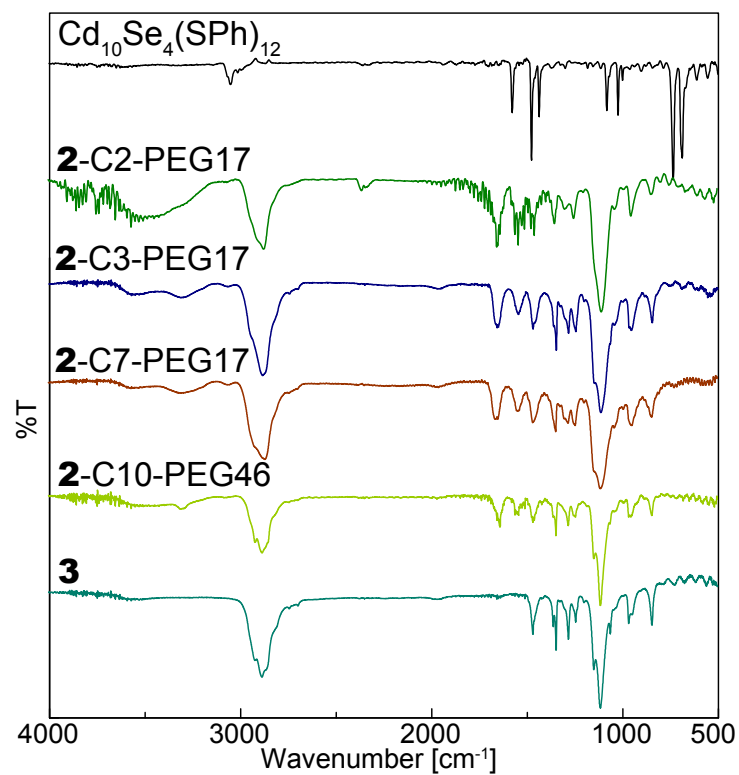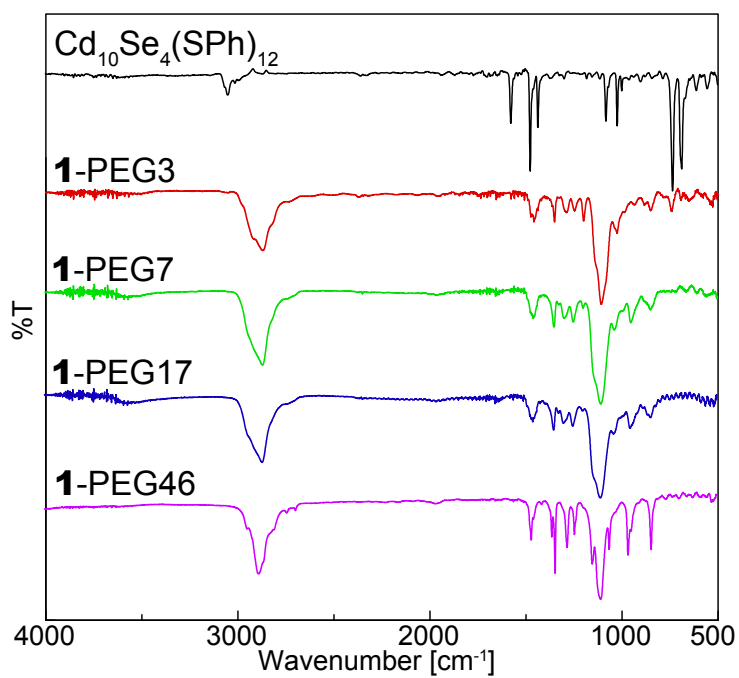
Fig. S1 FT-IR spectra in KBr pellets.

1-PEG3

1-PEG7

1-PEG17

1-PEG46

2-C2-PEG17

2-C3-PEG17

2-C7-PEG17

2-C10-PEG17
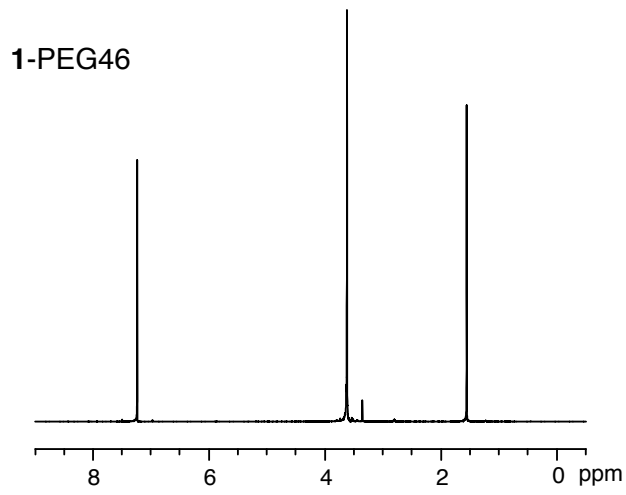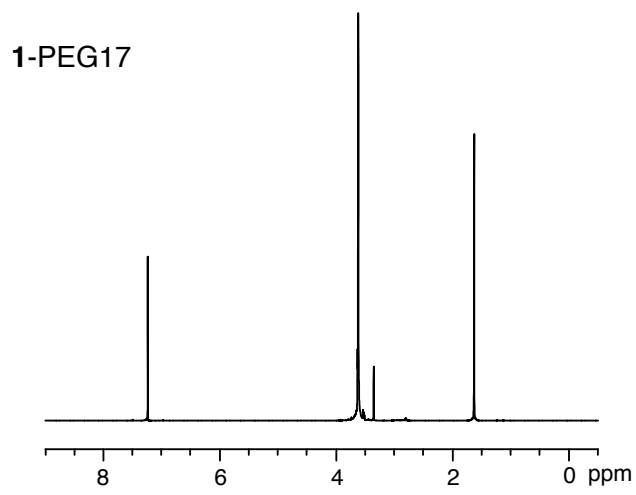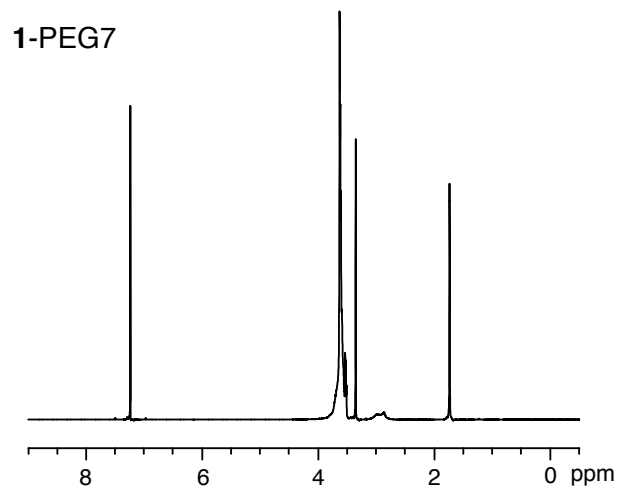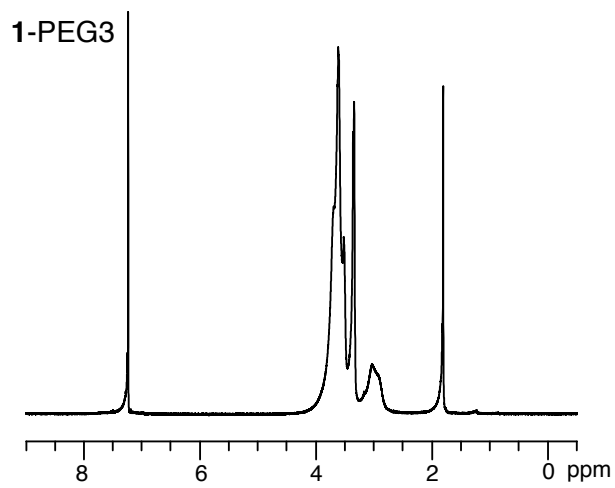
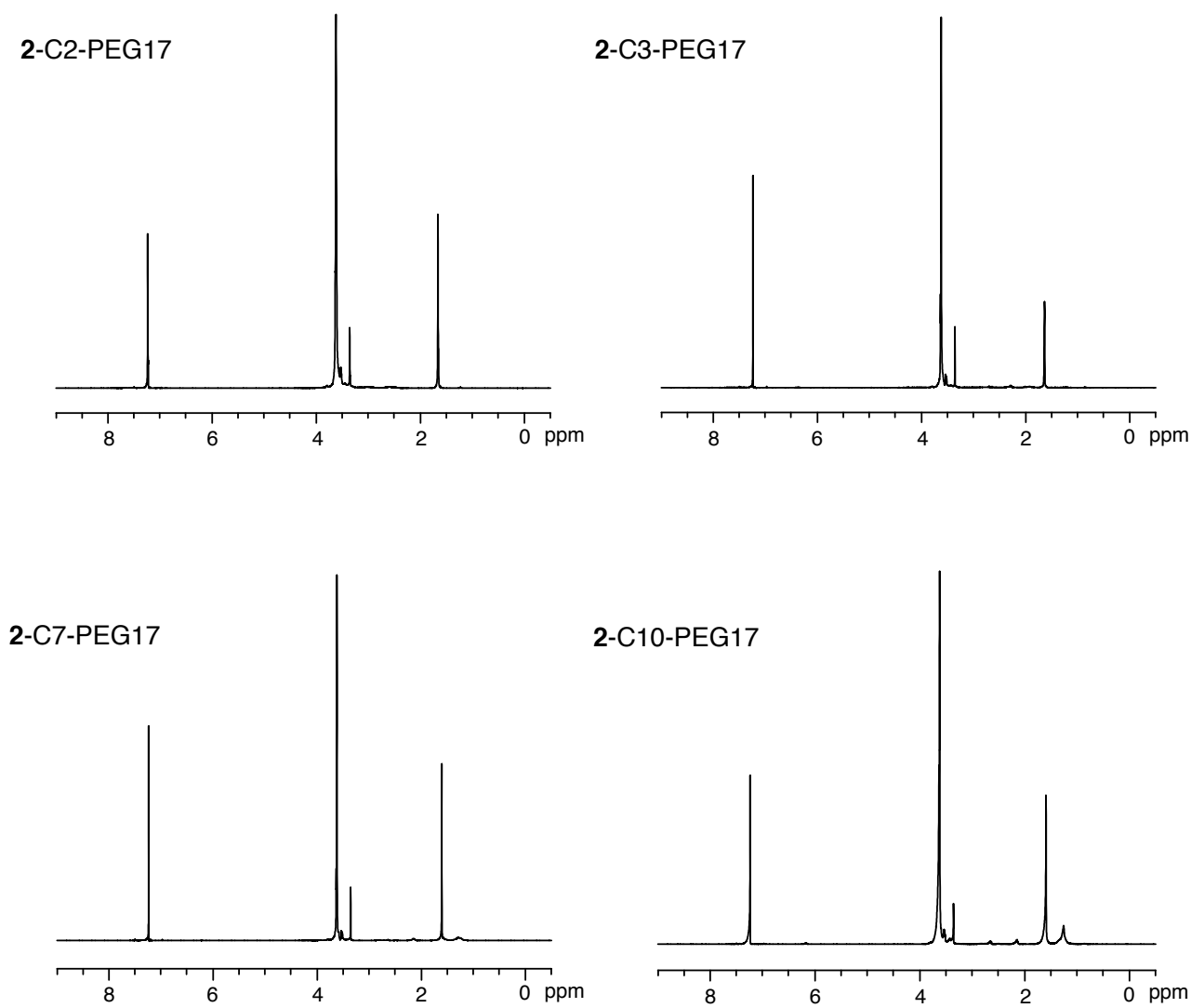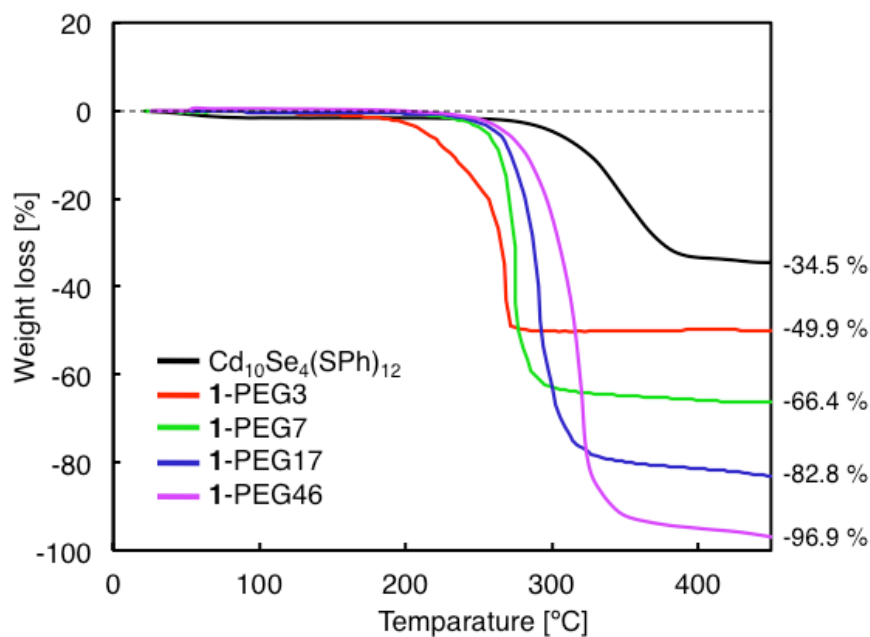**Fig. S2** ^{1}H NMR spectra in CDCl$_3$, r.t..

Fig. S3 Thermogravimetric (TG) profiles of $Cd_{10}Se_4(SPh)_{12}$ and **1**-PEGn (n = 3, 7, 17 and 46).

Table S1 Calculated and observed weight losses of $Cd_{10}Se_4(SR)_{12}$ clusters upon heated to 450 °C assuming the loss of organic moieties.

	Obsd. weight loss [%]	Calcd. weight loss [%]
$Cd_{10}Se_4(SPh)_{12}$	-34.5	-33.7
1-PEG3	-49.9	-49.2
1-PEG7	-66.4	-68.0
1-PEG17	-82.8	-83.2
1-PEG46	-96.9	-93.1
2-C2-PEG17	-87.3	-84.6
2-C3-PEG17	-83.7	-84.8
2-C7-PEG17	-89.6	-85.6
2-C10-PEG17	-87.4	-86.1
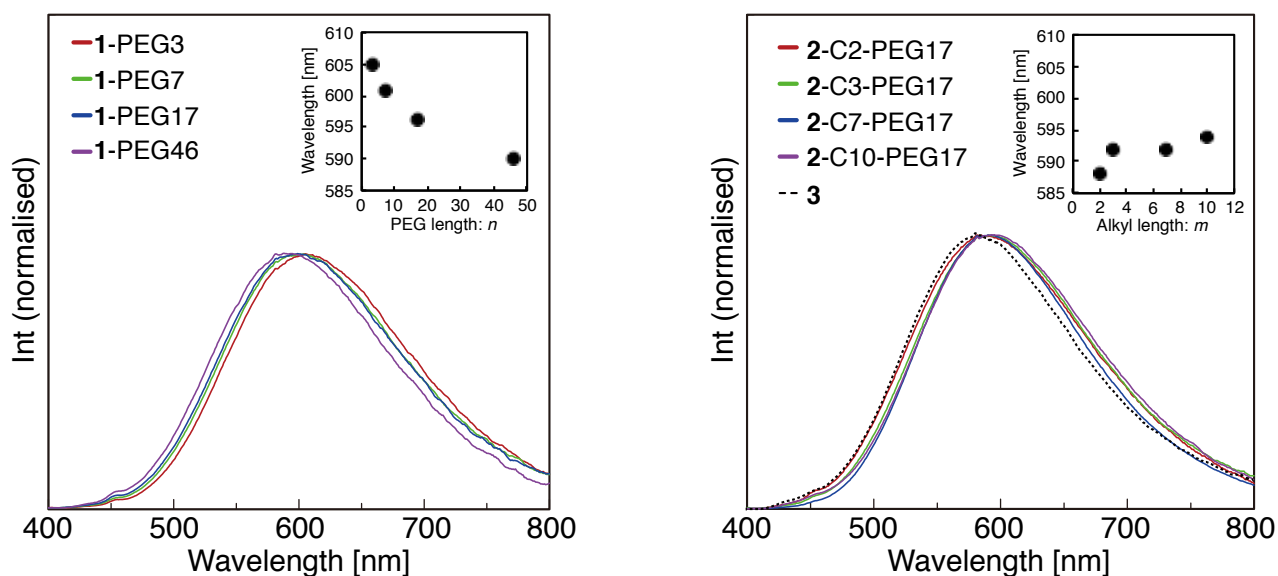
Fig. S4 Corrected photoluminescence emission (PL) spectra (λ_{ex} = 393 nm) of **1** - **3** in water at 20 °C. The intensities are normalised at the band maxima. Insets represent the plots of the wavelengths of the maxima versus PEG-chain length of **1** (a) and versus the alkyl-chain length of **2** (b).
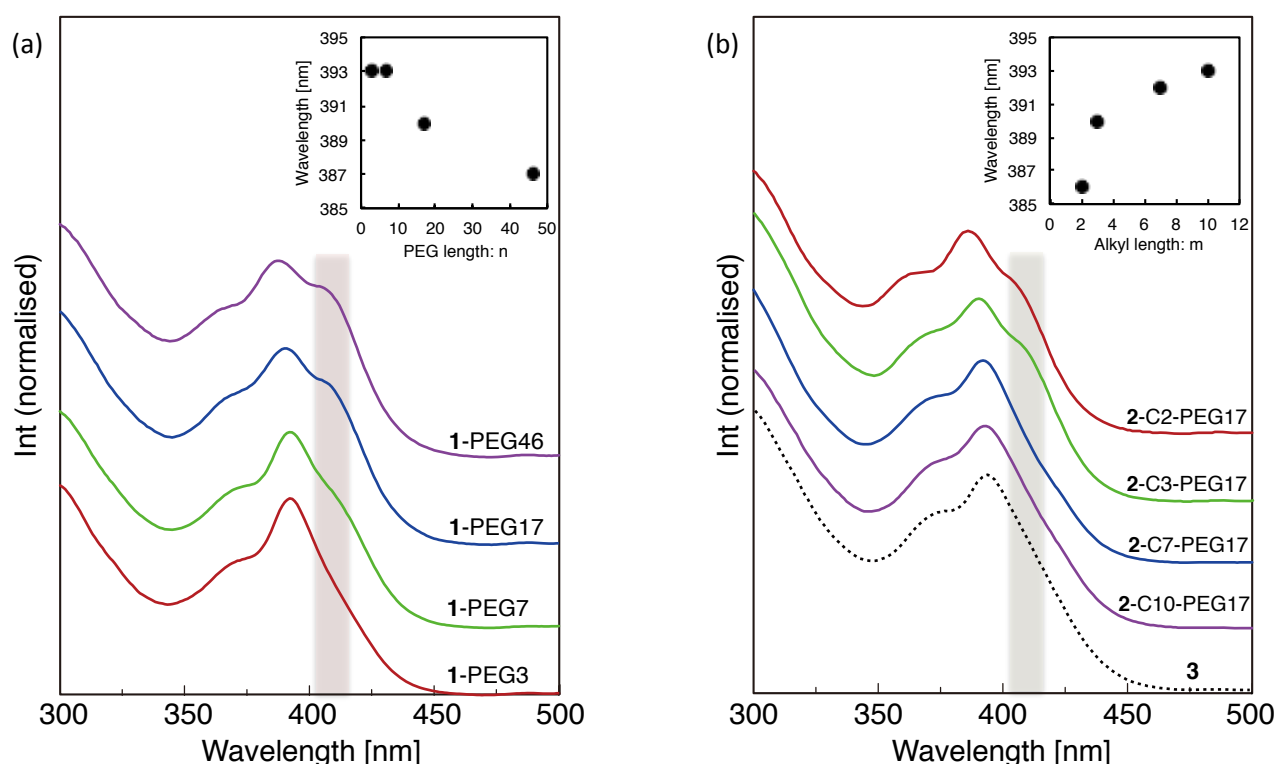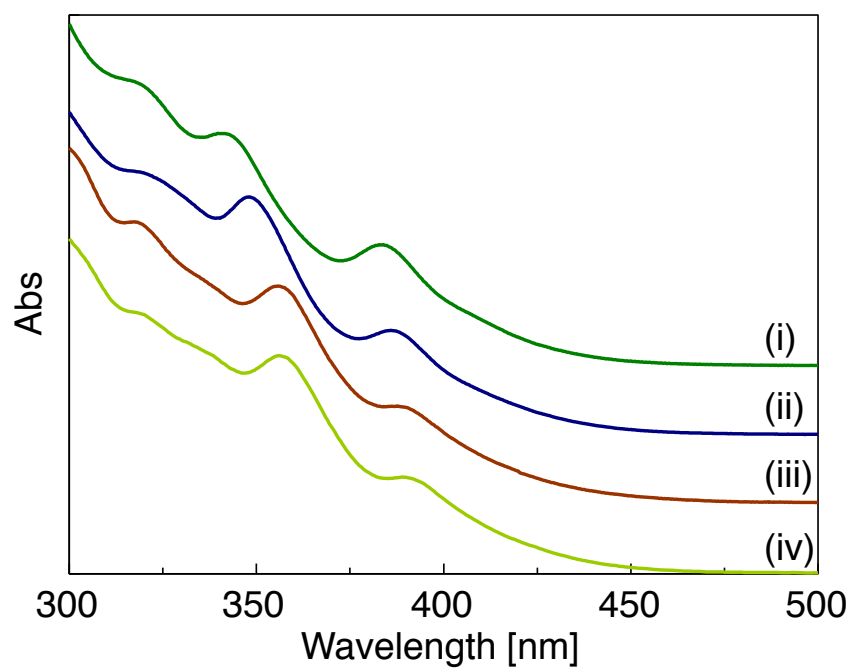

Fig. S5 Corrected photoluminescence excitation (PLE) spectra (monitored at 580 nm) of **1** - **3** in water at 20 °C. The intensities are normalised at the band maxima at ~390 nm. Insets represent the plots of the wavelengths of the maxima versus PEG-chain length of **1** (a) and versus the alkyl-chain length of **2** (b).

Fig. S6 Absorption spectra of (i) **2**-C2-PEG17, (ii) **2**-C3-PEG17, (iii) **2**-C7-PEG17, (iv) **2**-C10-PEG17, and **3** in water at 20 °C.
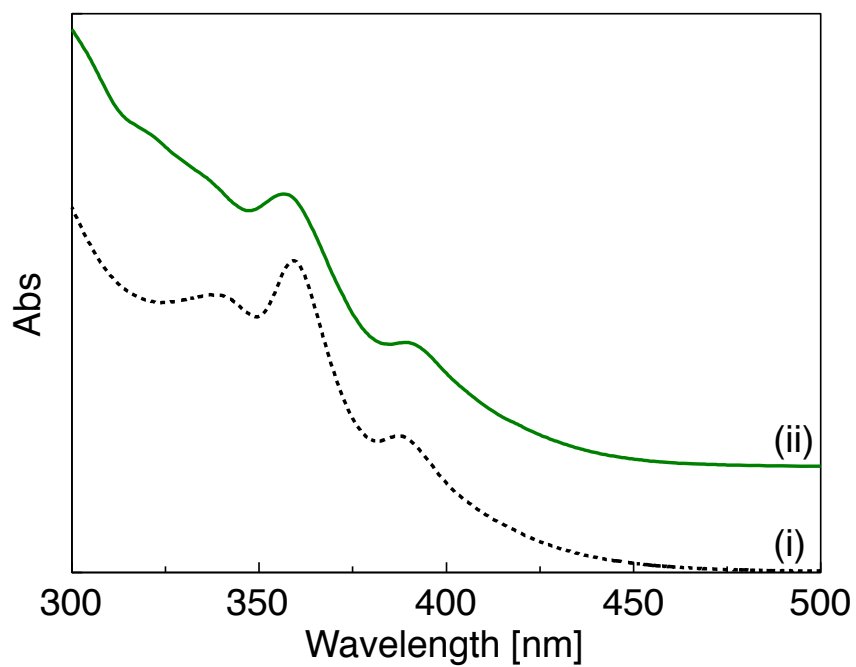

Fig. S7 Absorption spectra of (i) **1**-PEG3 and (ii) **3** in water at 20 °C.

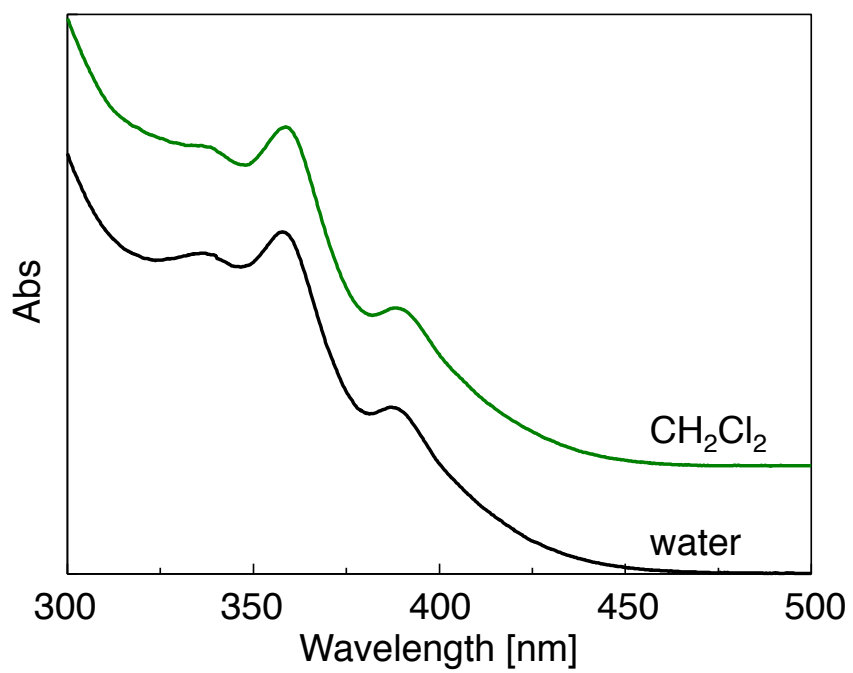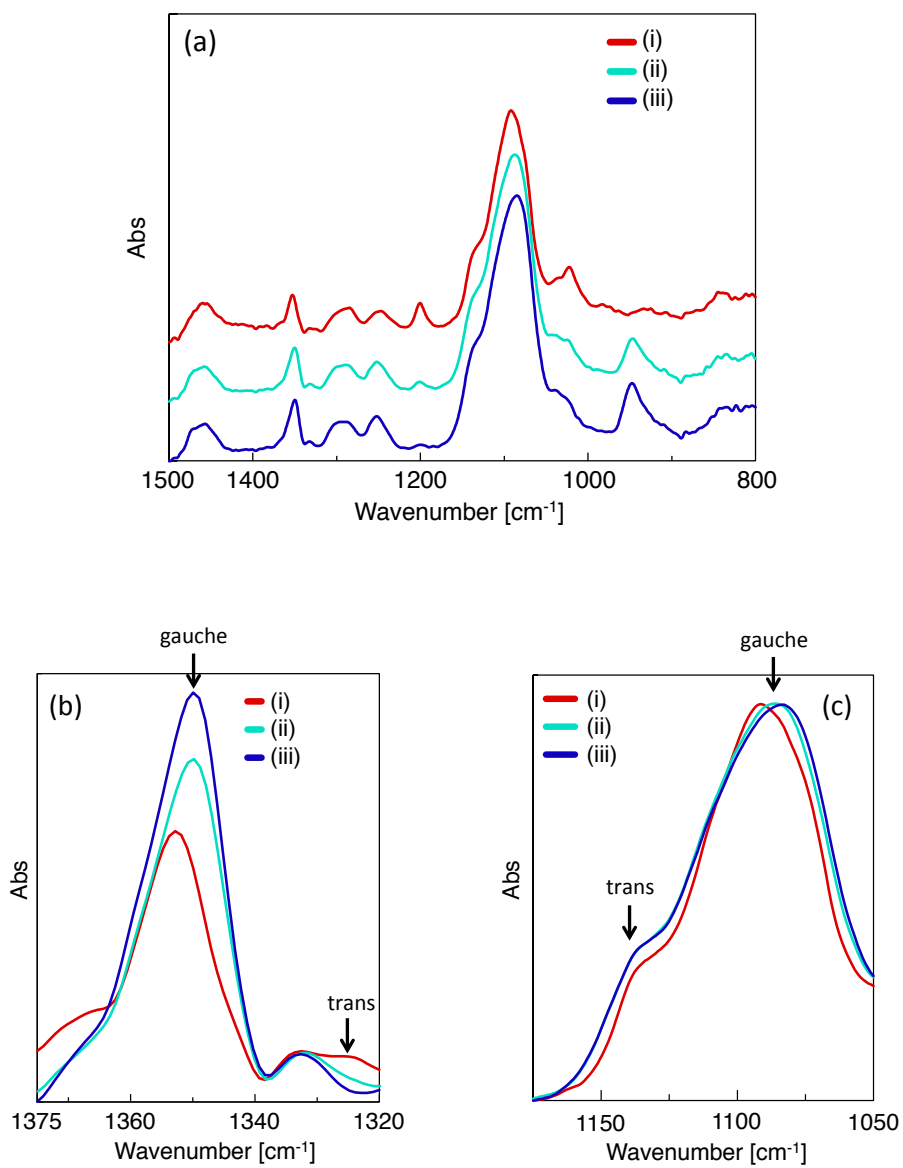**Fig. S8** Absorption spectra of **1**-PEG3 in water and CH_2Cl_2 at 20°C.

Fig. S9 ATR-IR spectra of (i) **1**-PEG3, (ii) **1**-PEG7 and (iii) **1**-PEG17 in water.