Supplementary Material (ESI) for Journal of Materials Chemistry

Supplementary

Surface-modified Nanoparticles via thermal and Cu(I)-mediated "click"-Chemistry: Generation of luminescent CdSe Nanoparticles with Polar Ligands Guiding Supramolecular Recognition

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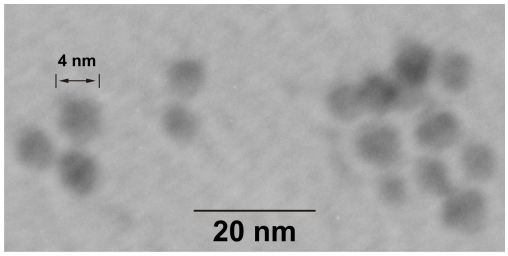


Fig. S1. Determination of the size of CdSe NPs via TEM.

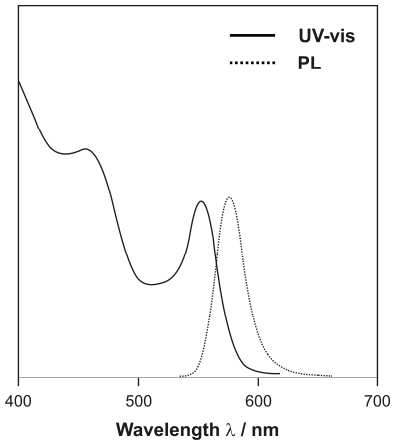
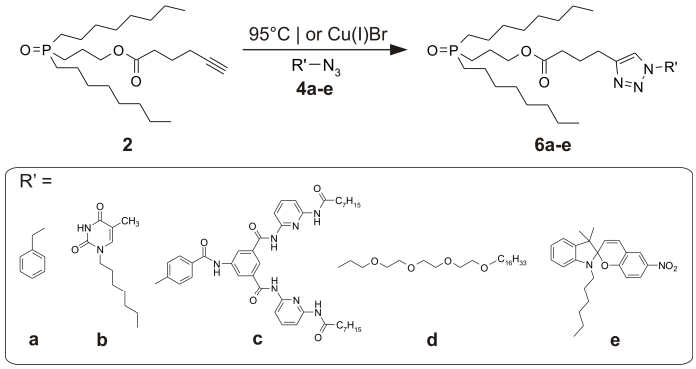


Fig. S2. UV-vis and photoluminescence (PL) spectra of **TOPO-NP**.

Synthesis of **6a-e** via "click" reaction

Synthesis of **6a-e** was conducted either Cu(I)-mediated (**C**) or purely thermal (**D**) (see Scheme S1).
General procedure **C**: Alkyne **2** (1 equiv.), azides **4a-e** (1.1 equiv.), N-ethyldiisopropylamine (DIPEA) (1.1 equiv.), *tris*-(benzyltriazolylmethyl)amine (TBTA)[1] (0.1 equiv.) and Cu(I)Br (0.1 equiv.) were dissolved in THF and stirred at 50°C. After 10 hours the reaction mixture was cooled to room temperature and the solvent was evaporated at reduced pressure. Purification of the residue by column chromatography on silica gel yielded the adducts **6a-e** in quantitative yields.
General procedure **D**: Alkyne **2** (1 equiv.) and azides **4a-e** (1.5 equiv.) were dissolved in toluene and stirred for 72 hours at 95°C. After evaporation of the solvent, the residue was purified by column chromatography on silica gel yielding an inseparable mixture of regioisomers of the adducts **6a-e** in quantitative yields.



Scheme S1. Synthetic pathway to prepare the "click" products **6a-e** by either thermal (95 °C) or Cu(I)-mediated 1,3-dipolar cycloaddition reactions.

4-(1-Benzyl-1H-[1,2,3]triazol-4-yl)-butyric acid 3-(dioctyl-phosphinoyl)-propyl ester (**6a**). Synthesis was accomplished with alkyne **2** (100 mg, 0.23 mmol) and azide **4a**[2] (34.3 mg, 0.26 mmol) according to the general procedure **C**. Purification by column chromatography on silica gel ($CHCl_3$:CH_3OH = 40:1) afforded the desired compound **6a** as a yellow oil (125 mg, 95%). Synthesis via general procedure **D** furnished an inseparable mixture of regioisomers. Data for **6a**: δ_H (400 MHz; $CDCl_3$; Me_4Si) 7.50-7.00 (m, 6H), 5.45 (s, 2H), 4.06 (m, 2H), 2.69 (m, 2H), 2.33 (m, 2H), 2.05-1.10 (m, 34H), 0.82 (m, 6H); δ_C (50 MHz; $CDCl_3$; Me_4Si) 171.60, 140.77, 139.60, 122.69, 122.59, 68.37 (d, $^3J_{PC}$ = 14.7 Hz), 54.48, 32.88, 31.92, 31.15 (d, $^3J_{PC}$ = 13.5 Hz), 29.04, 28.92, 27.93 (d, $^1J_{PC}$ = 64.9 Hz), 24.53 (d, $^1J_{PC}$ = 65.1 Hz), 23.45, 22.61, 21.63, 21.18, 18.01, 13.97; δ_P (162 MHz, $CDCl_3$; H_3PO_4) 49.28;

4-{1-[5-(5-Methyl-2,4-dioxo-3,4-dihydro-2H-pyrimidin-1-yl)-pentyl]-1H-[1,2,3]triazol-4-yl}-butyric acid 3-(dioctyl-phospinoyl)-propyl ester (**6b**). Synthesis was accomplished with alkyne **2** (100 mg, 0.23 mmol) and azide **4b**[3] (61.1 mg, 0.26 mmol) according to the general procedure **C**. Purification by column chromatography on silica gel ($CHCl_3$:CH_3OH = 30:1) gave titled product **6b** as a clear oil (143 mg, 92%). Synthesis via general procedure **D** furnished an inseparable mixture of regioisomers. Data for **6b**: δ_H (200 MHz; $CDCl_3$; Me_4Si) 9.13 (s, 1H), 7.34 (s, 1H), 6.96 (s, 1H), 4.31 (t, *J* = 6.7 Hz, 2H), 4.11 (t, *J* = 6.2 Hz, 2H), 3.65 (t, *J* = 7.5 Hz, 2H), 2.75 (m, 2H), 2.36 (t, *J* = 7.0 Hz, 2H), 2.10-1.05 (m, 41 H), 0.85 (t, *J* = 6.4 Hz, 6H); δ_C (50 MHz; $CDCl_3$; Me_4Si) 173.16, 164.09, 150.80, 140.25, 121.05, 110.65, 64.44 (d, $^3J_{PC}$ = 14.1 Hz), 50.01, 48.12, 33.37, 31.73, 31.11 (d, $^3J_{PC}$ = 13.8 Hz), 29.96, 29.01, 28.76, 27.93 (d, $^1J_{PC}$ = 64.8 Hz), 25.88, 25.65, 24.78, 24.53, 24.39 (d, $^1J_{PC}$ = 65.1 Hz), 22.58, 21.66, 21.18, 14.05, 12.30; δ_P (162 MHz, $CDCl_3$; H_3PO_4) 49.84;

4-(1-{4-[3,5-Bis-(6-octanoylamino-pyridin-2-ylcarbamoyl)-phenylcarbamoyl]-phenyl}-1H-[1,2,3]triazol-4-yl)-butyric acid 3-(dioctyl-phosphinoyl)-propyl ester (**6c**). Synthesis was accomplished with alkyne **2** (100 mg, 0.23 mmol) and azide **4c**[4] (196.2 mg, 0.26 mmol) according to the general procedure **C**. After purification by column chromatography on silica gel ($CHCl_3$:CH_3OH = 30:1), compound **6c** was obtained as a pale brown solid (253 mg, 91%). Synthesis via general procedure **D** furnished an inseparable mixture of regioisomers. Data for **6c**: δ_H (200 MHz; $CDCl_3$; Me_4Si) 10.22 (s, 1H), 9.20-8.25 (m, 4H), 8.15-7.40 (m, 14H), 4.10 (m, 2H), 2.79 (m, 2H), 2.65-2.25 (m, 8H), 2.15-1.05 (m, 52H), 0.83 (m, 12H); δ_C (50 MHz; $CDCl_3$; Me_4Si) 173.12, 172.81, 165.56, 164.47, 150.17, 149.12, 148.08, 140.31, 139.26, 134.88, 133.25, 129.52, 122.79, 119.38, 122.79, 119.38, 110.24, 109.42, 64.44 (d, $^3J_{PC}$ = 14.9 Hz), 37.42, 33.26, 31.69, 31.07 (d, $^3J_{PC}$ = 13.0 Hz), 29.23, 29.02, 27.76 (d, $^1J_{PC}$ = 65.1 Hz), 25.37, 24.68, 24.45 (d, $^1J_{PC}$ = 64.9 Hz), 24.22, 22.56, 21.70, 21.22, 14.03; δ_P (162 MHz, $CDCl_3$; H_3PO_4) 50.72;

4-[1-(2-{2-[2-(2-Hexadecyloxy-ethoxy)-ethoxy]-ethoxy}-ethyl}-1H-[1,2,3]triazol-4-yl)-butyric acid 3-octylphosphinoyl-decyl ester (**6d**). Synthesis was accomplished with alkyne **2** (100 mg, 0.23 mmol) and azide **4d**[5] (114.4 mg, 0.26 mmol) according to the general procedure **C**. Purification by column chromatography on silica gel ($CHCl_3$:CH_3OH = 40:1) furnished the desired compound **6d** as a pale green viscous liquid (184 mg, 92%). Synthesis via general procedure **D** furnished an inseparable mixture of regioisomers. Data for **6d**: δ_H (200 MHz; $CDCl_3$; Me_4Si) 7.50 (s, 1H), 4.47 (t, *J* = 4.3 Hz, 2H), 4.08 (t, *J* = 5.4 Hz, 2H), 3.82 (t, *J* = 4.3 Hz, 2H), 3.58 (m, 12H), 3.39 (t, *J* = 6.7 Hz, 2H), 2.72 (m, 2H), 2.35 (m, 2H), 2.10-1.10 (m, 62H), 0.83 (m, 9H); δ_C (50 MHz; $CDCl_3$; Me_4Si) 173.06, 71.43, 70.44, 69.89, 69.36, 64.42, 50.32, 33.33, 31.79, 31.65, 31.07, 29.56, 29.49, 29.37, 29.23, 28.97, 28.94, 25.96, 24.84, 24.34, 22.56, 22.50, 21.62, 21.12, 13.97; δ_P (162 MHz, $CDCl_3$; H_3PO_4) 49.14;

(**6e**). Synthesis was accomplished with alkyne **2** (100 mg, 0.23 mmol) and azide **4e**[6] (109.1 mg, 0.26 mmol) according to the general procedure **C**. Purification by column chromatography on silica gel ($CHCl_3$:CH_3OH = 40:1) afforded the desired compound **6e** as a purple solid (177 mg, 91%). Synthesis via general procedure **D** furnished an inseparable mixture of regioisomers. Data for **6e**: δ_H (200 MHz; $CDCl_3$; Me_4Si) 8.01-7.95 (m, 2H), 7.35-6.85 (m, 5H), 6.72 (d, J = 9.6 Hz, 1H), 5.80 (d, J = 10.1 Hz, 1H), 4.12 (t, J = 6.4 Hz, 2H), 3.68 (m, 2H), 3.17 (m, 2H), 2.70 (m, 2H), 2.34 (m, 2H), 2.05-1.05 (m, 46H), 0.86 (m, 6H); δ_C (50 MHz; $CDCl_3$; Me_4Si) 173.25, 159.56, 146.89, 141.12, 140.80, 136.11, 128.12, 127.46, 125.53, 122.61, 121.89, 121.53, 121.26, 119.19, 118.31, 115.32, 106.52, 64,38 (d, $^3J_{PC}$ = 14.3 Hz), 51.31, 51.11, 43.53, 33.42, 31.73, 31.06 (d, $^3J_{PC}$ = 13.9 Hz), 29.06, 28.79, 28.72, 27.91 (d, $^1J_{PC}$ = 65.1 Hz), 25.86, 24.42, 24.33 (d, $^1J_{PC}$ = 64.8 Hz), 23.31, 22.59, 21.64, 19.76, 13.87;

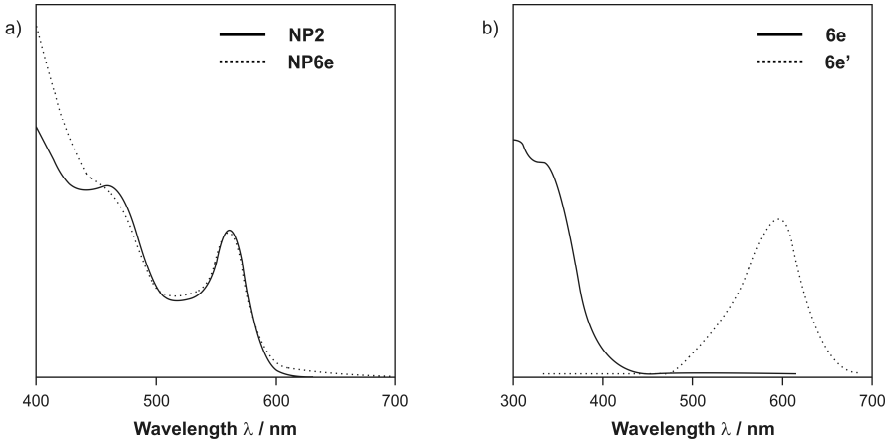


Fig. S3. UV-vis spectra of a) **NP2** and **NP6e** and b) the spiropyran **6e** and its mero isomers **6e'**.

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