

## An “Off-On” Sensor for Fluoride Using Luminescent CdSe/ZnS Quantum Dots

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### *Materials and Reagents*

Chemicals were purchased from Aldrich Co. and used as received without further purification. Green emitting CdSe-ZnS QD's were purchased from Evident Technologies, New York (product No ED-C10-TOL-0545). Ferrocene methyl amine was prepared following a literature procedure.<sup>1</sup> The <sup>1</sup>H and <sup>13</sup>C NMR spectra and the mass spectrum are presented in Fig's S4 and S5.

### *Synthesis of 1*

Based on a procedure by Fidesser et al<sup>2</sup>, an ice cold solution of thioctic acid (3.80 g, 18.5 mmol) and triethylamine (1.87 g, 18.5 mmol) in dry DMF was stirred for 10 mins, after which a solution of diphenylphosphoryl azide (5.10 g, 18.5 mmol) in dry DMF (15 mL) was added dropwise over a period of 2 hrs. After removal of the ice bath, stirring was continued for 3 hrs at room temperature. The reaction contents were then poured into a mixture of diethyl ether and ice. When the ice had thawed, the ether layer was collected and washed with a saturated solution of NaHCO<sub>3</sub>. This was then washed with H<sub>2</sub>O, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and the solvent evaporated under reduced pressure (bath temperature not exceeding 30 °C to afford the product). Yield = 2.93 g (68.6 %). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 1.45 (m, 2H, CHCH<sub>2</sub>), 1.65 (m, 4H, 2 x CH<sub>2</sub>), 1.88 (m, 1H, ring CH<sub>2</sub>), 2.33 (t, *J* = 7.2 Hz, 2H, CH<sub>2</sub>C=O), 2.44 (m, 1H, ring CH<sub>2</sub>), 3.12 (m, 2H, S-CH<sub>2</sub>), 3.54 (m, 1H, S-CH). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 24.41 (CH<sub>2</sub>), 28.58 (CH<sub>2</sub>), 34.56 (CH<sub>2</sub>C=O), 36.60 (CHCH<sub>2</sub>), 38.52 (S-CH<sub>2</sub>), 40.22 (CH-CH<sub>2</sub>), 56.23 (CH), 180.40 (C=O). I.R. (Nujol) 2138 cm<sup>-1</sup> (N<sub>3</sub>). *m/z* (ESMS) 276.0 (M<sup>+</sup> + 2Na - H) (75%), 239 (100%).

### *Synthesis of 3.*

A solution of **1** (1.85 g, 8 mmol) in dry toluene (100 mL) was refluxed for 15 mins under N<sub>2</sub> to form **2**. Without isolation of **2**, ferrocenemethylamine (1.74 g, 8 mmol) in dry toluene (10 mL) was pipetted into the stirring solution. The mixture was refluxed for 2 hrs. The solvent was then removed under reduced pressure. The crude product was purified by flash chromatography (DCM / MeOH, 98:2) and solvent evaporated to give a dark orange oil. Yield = 3.2 g (95.7 %). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 1.47 (m, 4H, 2 x CH<sub>2</sub>), 1.65 (m, 2H, CH<sub>2</sub>), 1.88 (m, 1H, ring CH<sub>2</sub>), 2.39 (m, 1H, ring CH<sub>2</sub>), 3.07 (m, 2H, CH<sub>2</sub>-NH), 3.14 (m, 2H, S-CH<sub>2</sub>), 3.53 (m, 1H, CH), 4.03 (s, 2 H, CH<sub>2</sub>-C<sub>p</sub>), 4.03 (m, 2H, C<sub>p</sub>), 4.14 (s, 5H, C<sub>p</sub>), 4.18 (m, 2H, C<sub>p</sub>), 4.35 (br, 2H, NH). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 157.8, 85.7, 68.5, 68.1, 67.9, 56.5, 40.4, 40.3, 39.9, 38.5, 34.6, 30.3, 26.5. HRMS, calculated for C<sub>19</sub>H<sub>26</sub>ON<sub>2</sub>S<sub>2</sub>FeH: 419.0909 [M+H<sup>+</sup>]. Found: 419.0907.

### *Synthesis of 4.*

Based on a procedure by Chittiboyima *et al.*,<sup>3</sup> to an ice cold solution of 1-ferrocenyl-3-[4-(1,2-dithiolan-3-yl)butyl]urea (3.12 g, 7.5 mmol) in THF (200 mL), was added dropwise a solution of NaBH<sub>4</sub> (0.53 g, 14 mmol) in 15 mL of H<sub>2</sub>O. The mixture was allowed to stir at the same temperature for an additional 1 hr. After completion of the reaction, aqueous 1N HCl (37.5 mL) was added and the solvent was removed under reduced pressure (bath temp < 40 °C). The residue was diluted with H<sub>2</sub>O (100 mL) and extracted with DCM (2 x 200 mL). The combined organic layers were washed with brine, dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated under vacuum. Yield = 3.0 g (95.2 %). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 1.26 (d, 1H, *J* = 8 Hz, CH-SH), 1.33 (m, 1H, *J* = 8 Hz, CH<sub>2</sub>-SH), 1.47 (m, 4H, 2 x CH<sub>2</sub>), 1.65 (m, 2H, CH-CH<sub>2</sub>), 1.88 (m, 1H, ring CH<sub>2</sub>),

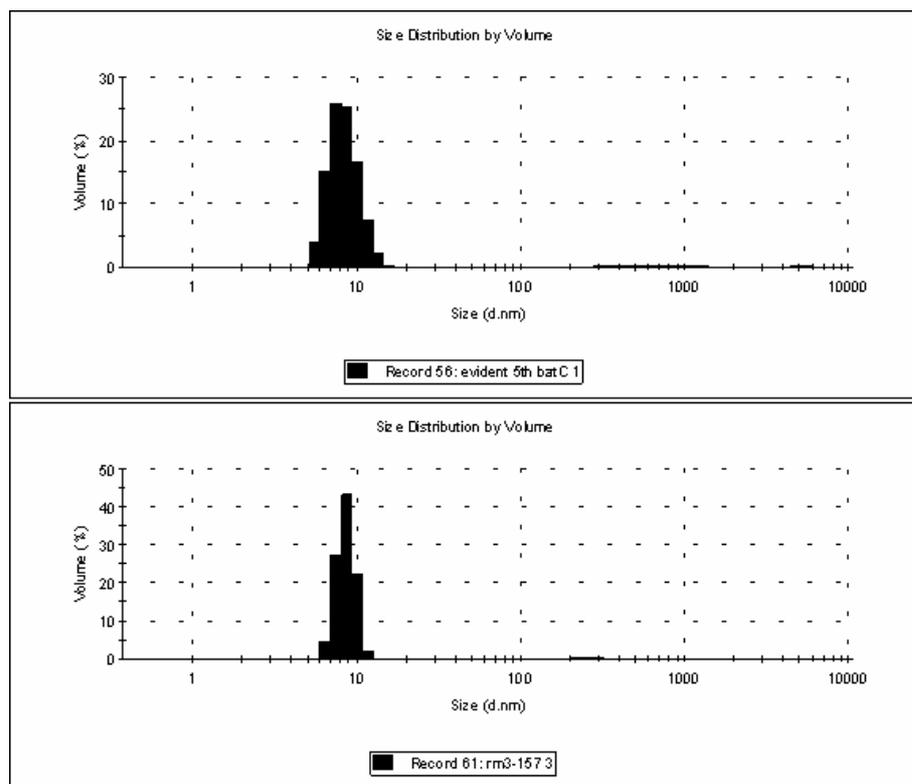
2.43 (m, 1H, ring  $CH_2$ ), 3.08 (m, 2H,  $CH_2$ -NH), 3.14 (m, 2H, S- $CH_2$ ), 3.53 (m, 1H, CH), 4.05 (s, 2 H,  $CH_2$ - $C_p$ ), 4.09 (m, 2H,  $C_p$ ), 4.13 (s, 5H,  $C_p$ ), 4.15 (m, 2H,  $C_p$ ).  $^{13}C$  NMR (100 MHz,  $CDCl_3$ ):  $\delta$  158.0, 85.8, 68.8, 68.0, 67.9, 56.5, 40.3, 40.3, 39.8, 38.5, 34.6, 29.9, 26.5.  $m/z$  (ESMS) 422 (10%), 421 (40%) ( $M^+$ ), 419 (100%), 417 (15%).

### *Synthesis of 5*

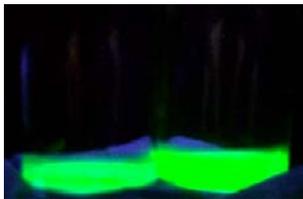
To a stirred solution of **4** (0.1 g, 0.24 mmol,) in  $CHCl_3$  (10 mL) under  $N_2$ , was added CdSe/ZnS QD's (2 mL,  $5.43 \times 10^{-6}$  moles). The solution was stirred at 60°C for 3 hours after which another aliquot of **4** (0.1 g, 0.24 mmol) was added. The resulting mixture was stirred overnight at ambient temperature. The solvent was removed under reduced pressure and the product reconstituted in acetonitrile. The slurry was centrifuged and the supernatant decanted off. This was repeated a further three times. The resulting pellets were dried in vacuo to yield an orange solid.

## **2. Experimental: Equipment and Parameters**

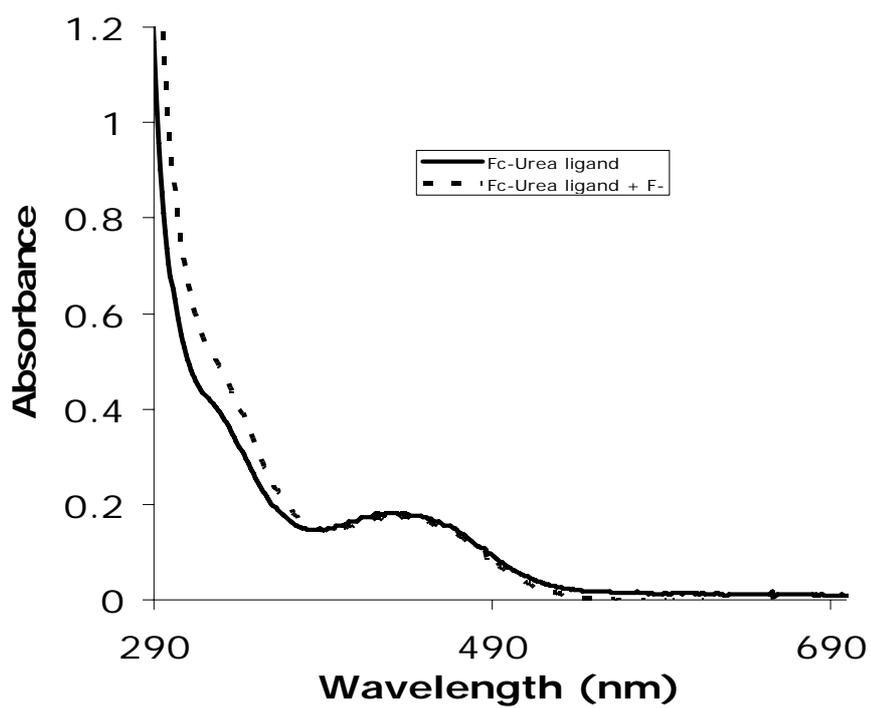
UV-Vis measurements were recorded on an Agilent UV-Vis Spectrometer using 10 mm quartz cuvettes. Fluorescence measurements were recorded on a Perkin Elmer LS55 Luminescence Spectrometer using 10 mm quartz cuvettes. Excitation wavelength unless otherwise stated was set at 370 nm. Excitation slit size was 10.0 nm and emission slit size was 10.0 nm. Scan speed was set at 500. NMR spectra were recorded on a Bruker Ultrashield 400 MHz. Chemical shifts are reported in parts per million ( $\delta$ ) downfield of TMS. Particle size distributions were recorded on a Malvern NanoZS instrument at 25°C in a 10 mm cuvette using a He-Ne laser of 633 nm. The average size is the average of 20 independent experiments and the standard deviation is taken as the error.



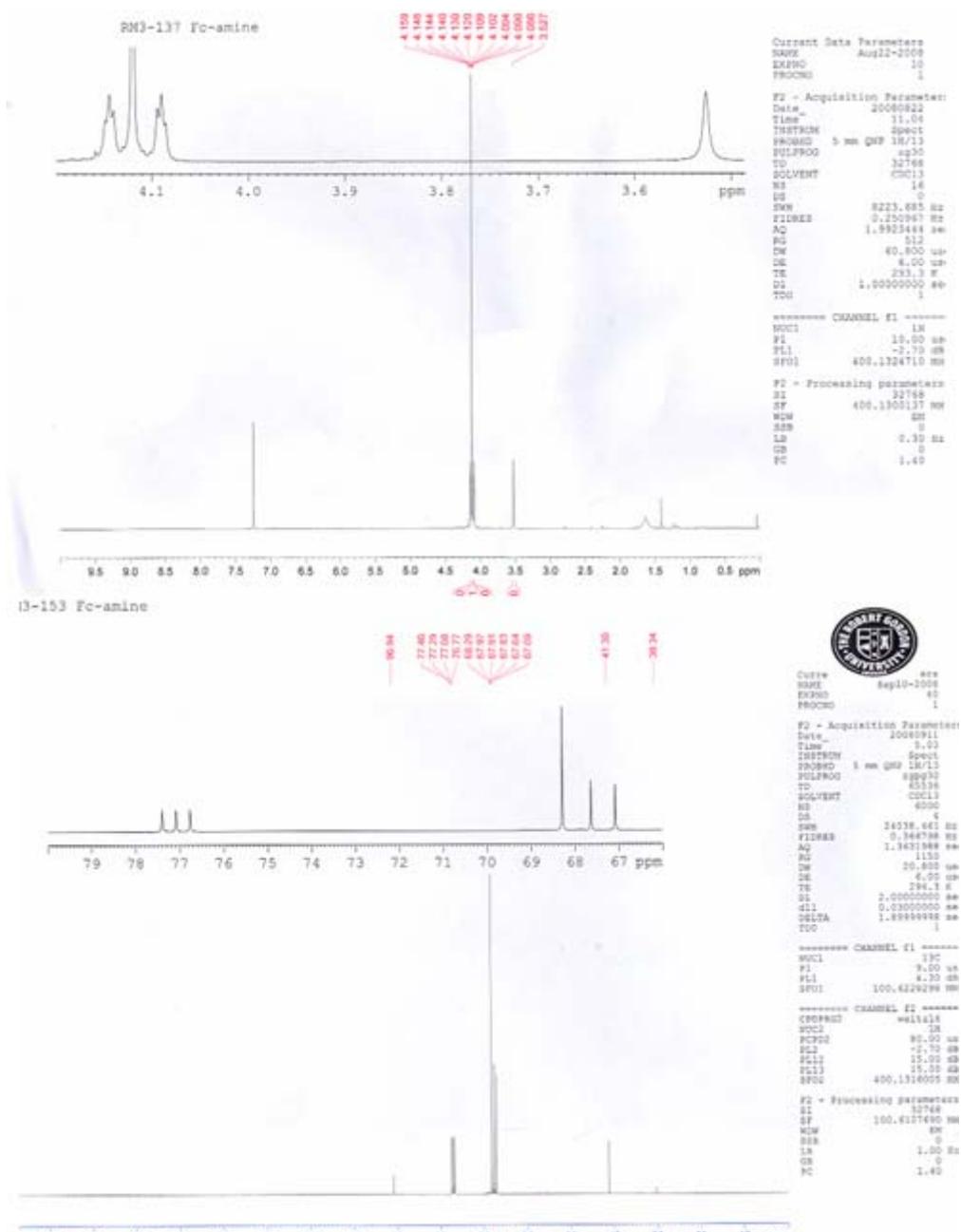
**Figure S1** Dynamic light scattering (DLS) profile of parent CdSe/ZnS QD's (top) and **5** (bottom) recorded in THF.



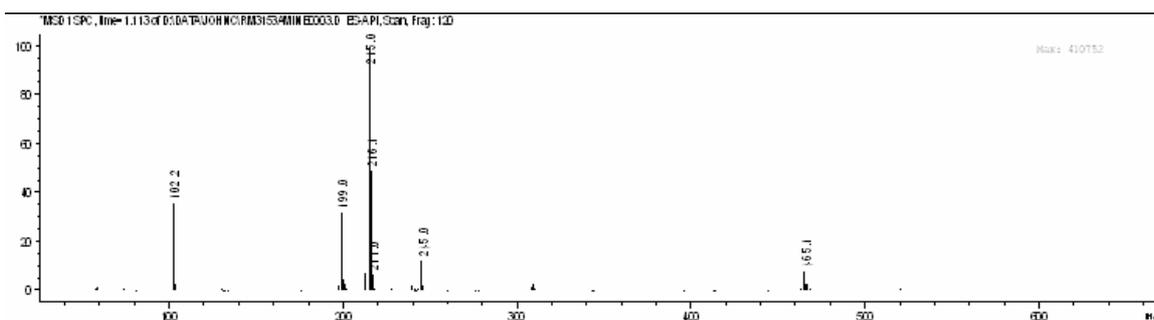
**Figure S2** Picture of parent CdSe/ZnS QD's (i.e. with no ferrocenyl urea attached) after being subjected to the same experimental conditions as were used in the conversion of **4** to **5**. Left hand vial is in the absence of fluoride and right hand vial is in the presence of fluoride.  $[\text{CdSe/ZnS QD's}] = 2 \times 10^{-6} \text{ M}$ ,  $[\text{F}^-] = 3.8 \times 10^{-2} \text{ M}$ .



**Figure S3** UV-Vis spectra of **4** in the absence (solid line) and in the presence (broken line) of fluoride.  $[4] = 2.4 \times 10^{-2}$  M,  $[F^-] = 1.9 \times 10^{-1}$  M.



**Figure S4**  $^1\text{H}$  (top) and  $^{13}\text{C}$  NMR (bottom) spectra of ferrocene methyl amine.



**Figure S5** Positive ESI mass spectrum of ferrocene methyl amine.

## References

1. A. Baramée, A. Coppin, M. Mortuaire, L. Pelinski, S. Tomavo and J. Brocard, *Bioorg. Med. Chem.*, 2006, **14**, 1294-1302.
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3. A. G. Chittiboyina, M. S. Venkatraman, C. S. Mizuno, P. V. Desai, A. Patny, S. C. Benson, C. I. Ho, T. W. Kurtz, H. A. Pershadsingh, M. A. Avery, *J. Med. Chem.* 2006, **49**, 4072-4084.