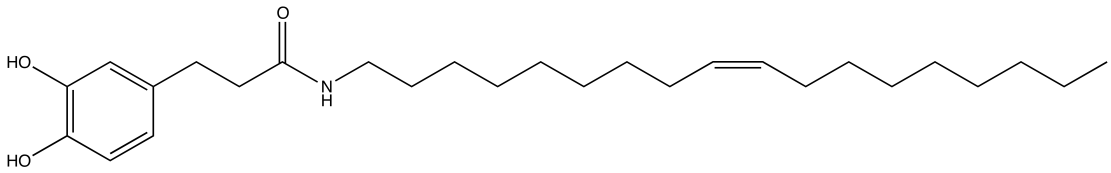
Electronic Supplementary Material (ESI) for RSC Advances.

Catechols as ligands for CdSe/ZnS quantum dots
Supporting information

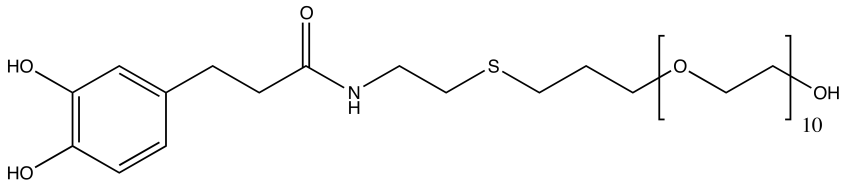
Synthesis of ligands

Catechol-C_{18}



Dihydroxy hydrocinnamic acid (4 mmol, 728.7 mg) was activated by CDI (4.4 mmol, 713.46 mg) in 3 ml of dry DMF. After 10 minutes oleylamine (4 mmol, 1.316 ml) was added. To improve the solubility of the oleylamine, 1 ml of dichloromethane was added. This mixture was stirred for 72 hours at room temperature before it was diluted by adding 5ml of dichloromethane. The organic phase was washed with an aqueous 1M NaOH solution (3 x 20 ml) and 1M HCl solution (3 x 20 ml). Finally the mixture was extracted with a saturated NaCl solution (3 x 20 ml) and dried with $MgSO_4$. After filtration, the solvent was removed under reduced pressure. The product was obtained as a light-yellow waxy solid (1.61 g, 93%). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 0.88 (t, 3H), 1.2-1.4 (m, 24H), 2.00 (m, 4H), 2.41 (q, 2H), 2.63 (t, 2H), 3.32 (t, 2H), 5.35 (m, 2H), 6.5-7.0 (m, 3H)

Catechol-PEG



First, via click chemistry, an amine group was introduced onto an allyl-PEG molecule, following the procedure published by Tucker *et al*.[1] Allyl-PEG10-OH (Polysciences, 2 mmol, 0.996 g) was mixed with dimethoxy phenyl acetophenone (0.1 mmol, 25 mg) and cysteamine (2 mmol, 154 mg) in 0.5 ml dry DMF. The mixture was sonicated for 5 minutes to dissolve cysteamine faster and irradiated with UV light (365 nm, 200 mW) for 2 hours. This product was used without further purification. Secondly, dihydroxy hydrocinnamic acid (2 mmol, 364.3 mg) was activated by CDI (2.2 mmol, 365.7 mg) in 1 ml of dry DMF. Both mixtures were combined after 10 minutes and stirred for 16 hours at room temperature. To purify the product, the mixture was added to cold diethylether (45 ml) and the white precipitate was collected via centrifugation (10000 rpm, 5 min). The product was obtained as a white waxy solid (1.12 g, 75%). ^{1}H NMR (400 MHz, D_2O): δ (ppm) 2.09 (t, 4H), 2.36 (q, 2H), 2.54 (t, 2H), 2.70 (t, 2H), 3.33-3.65 (m, 44H), 6.6-7.0 (m, 3H)

Photoluminescence data

The optical properties of the QDs modified with the C_{18} and PEG_{10} ligands can be found in the following section. Absorbance spectra were recorded with an Ultraspec 2100 Pro UV/visible spectrophotometer from GE Healthcare. Photoluminescence spectra were measured with a QuantaMaster™ 60 from Photon Technology International. The quantum yield values reported are absolute external quantum efficiencies (EQE) and were measured by using an Spectrolon integrating sphere coupled to a spectrofluorimeter (fluorolog FL3-22 from Horiba Jobin Yvon). The followed procedure, as well as the formula used to

calculate the EQE from the measurements, is described in detail by Coutino-Gonzalez *et al.* [2]

A clear influence of the catechol group on the quantum yield is visible: 24% for the original QD versus 0.5-1% for the catechol-modified QD.

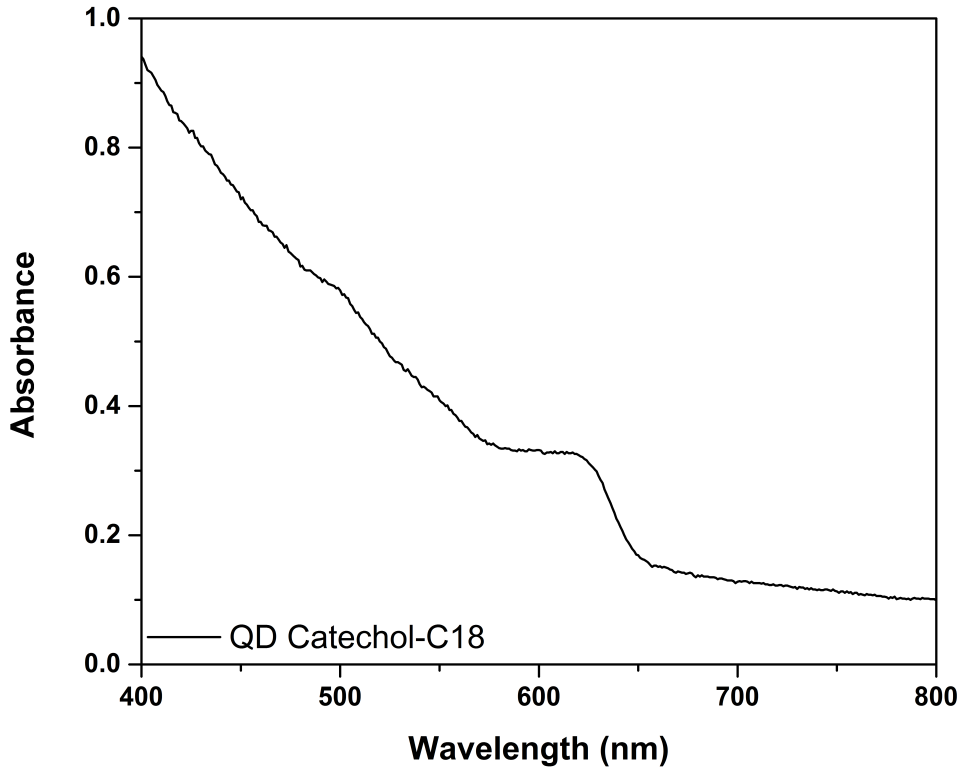


Figure S 1. Absorbance spectra of the catechol-C_{18} modified QD.

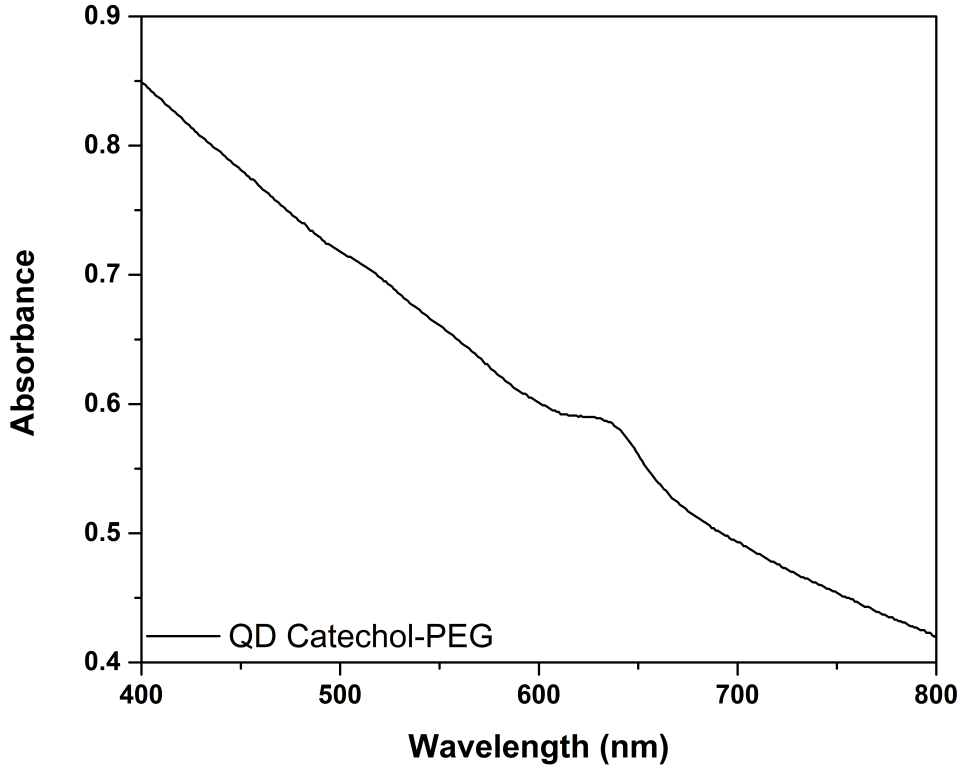


Figure S 2. Absorbance spectra of the catechol-PEG modified QD. Scattering of impurities or small aggregates likely causes the substantial background, present in the spectrum. The characteristic peaks of the quantum dot spectrum are however clearly visible in the spectrum, indicating their successful transfer.

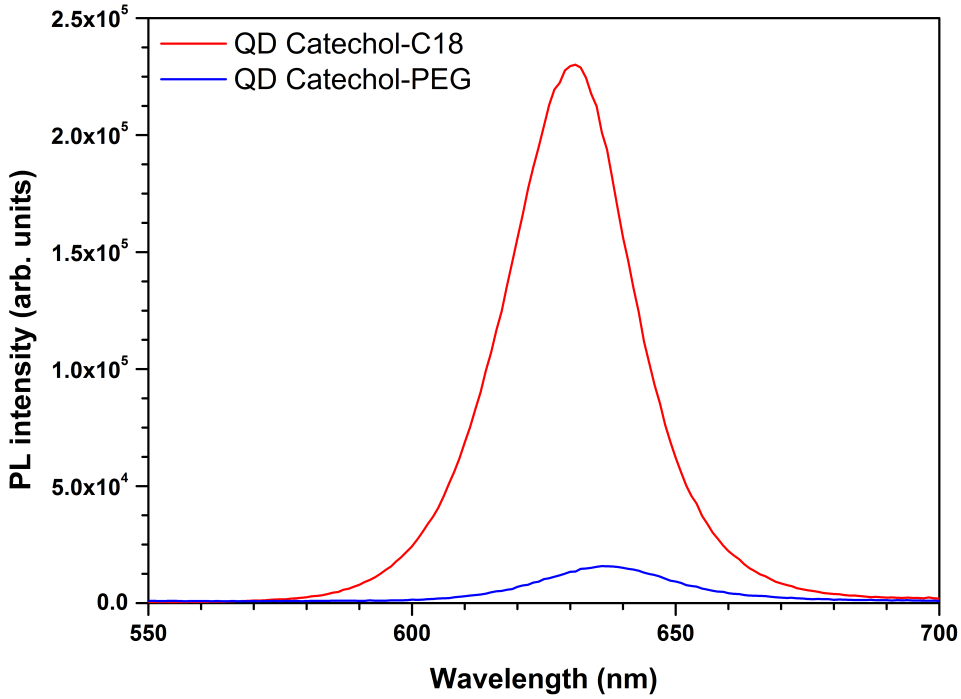


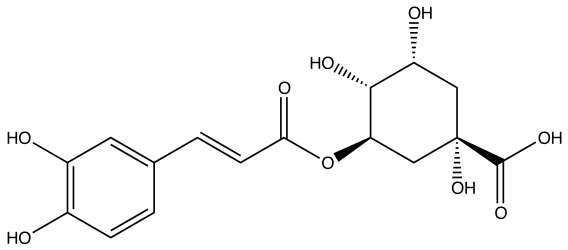
Figure S 3. Photoluminescence of the QD, modified with C_{18} and PEG catechol molecules.

Tabel S 1. Comparison of the quantum yield of the different QD samples

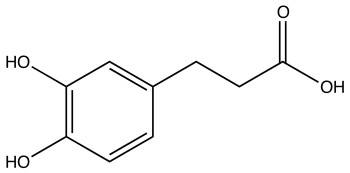
Sample	Quantum yield
Original QD	24%
Catechol-C_{18} modified QD	1.1%
Catechol-PEG_{10} modified QD	0.5%

Fourier transform infrared data

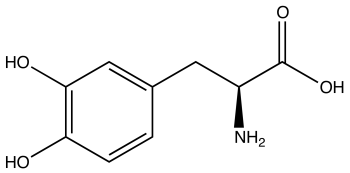
The FTIR spectra of all quantum dot-catechol samples, not shown in the paper, can be found in the following section. In total, four different commercially-obtained catechols were introduced onto the quantum dot's surface: chlorogenic acid (Figure S 5), dihydroxy phenylalanine (Figure S 6), dopamine (Figure S 7) and dihydroxy hydrocinnamic acid (Figure S 8). Figure S 4 shows the chemical structure of these molecules in more detail.



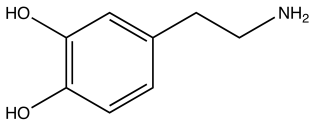
Chlorogenic acid



Dihydroxy hydrocinnamic acid



Dihydroxy phenylalanine



Dopamine

Figure S 4. Structure of the different catechol molecules

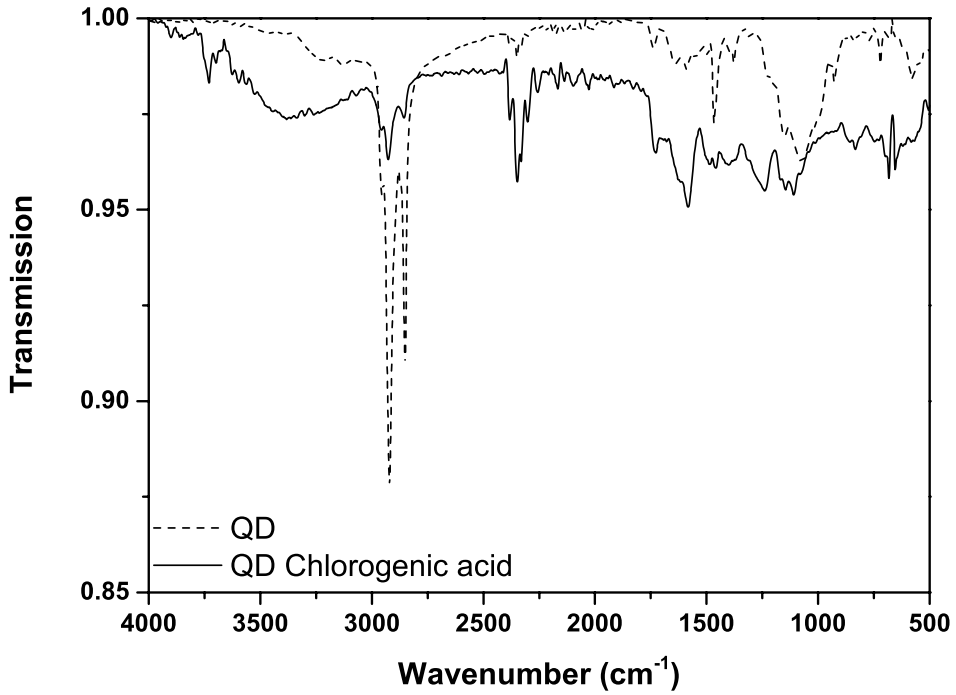


Figure S 5. FTIR spectrum of chlorogenic acid modified quantum dots

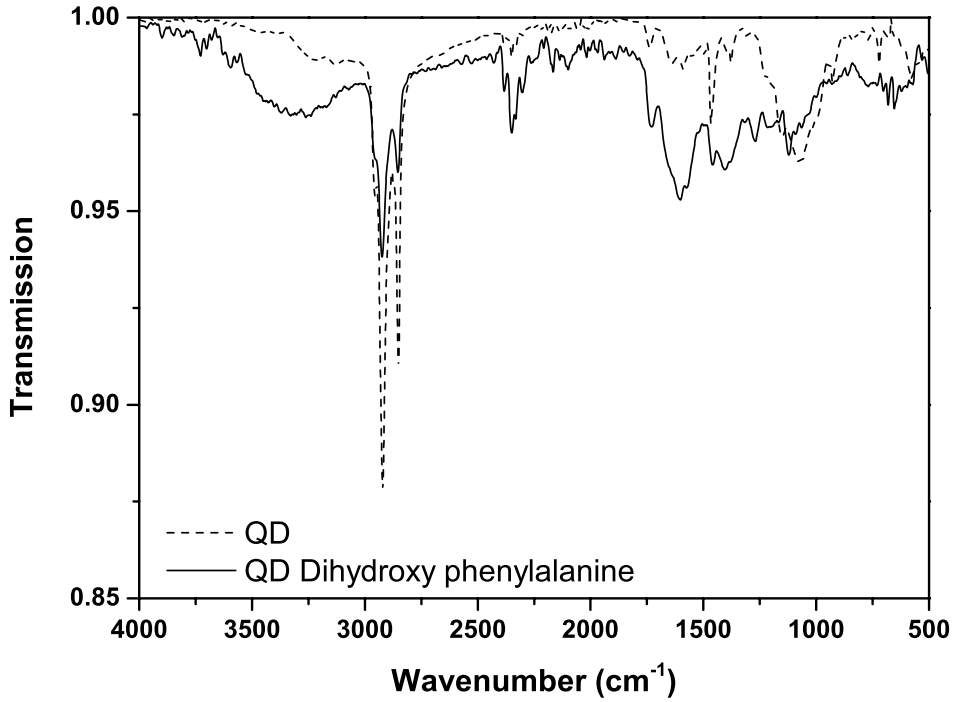


Figure S 6. FTIR spectrum of dihydroxy phenylalanine modified quantum dots

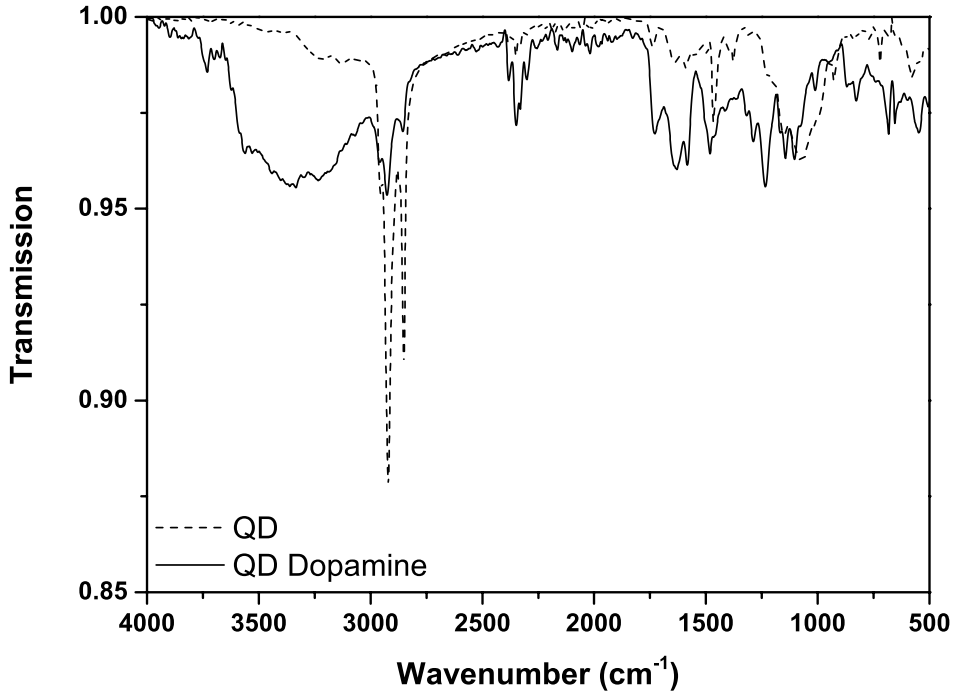


Figure S 7. FTIR spectrum of dopamine modified quantum dots

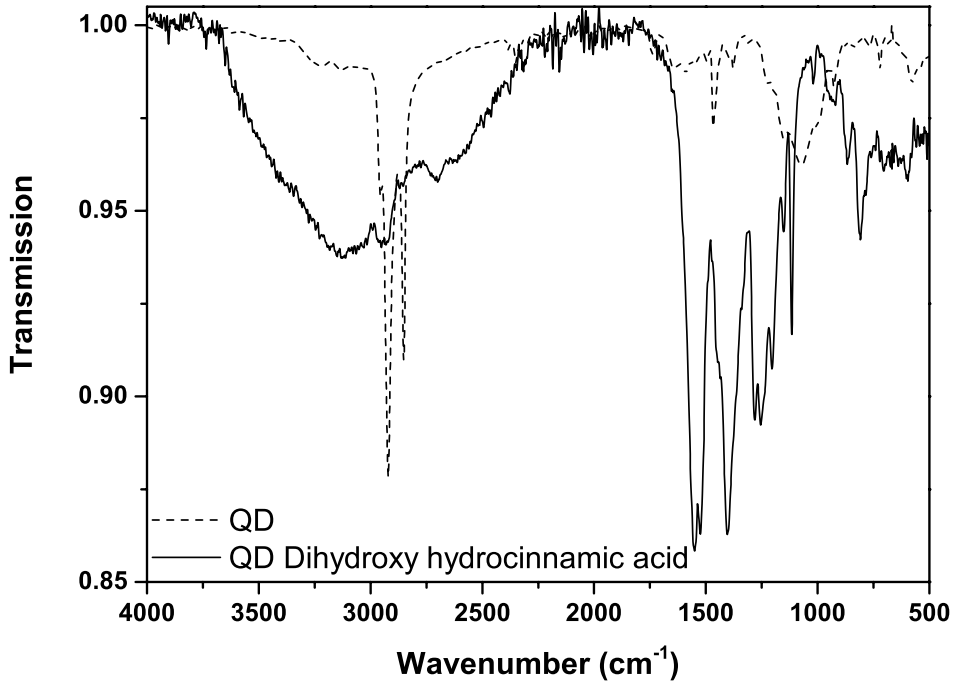


Figure S 8. FTIR spectrum of dihydroxy hydrocinnamic acid modified quantum dots

References

1. A. K. Tucker-Schwartz, R. a Farrell, and R. L. Garrell, *J. Am. Chem. Soc.*, 2011, **133**, 11026–9.

2. E. Coutino-Gonzalez, M. B. J. Roeffaers, B. Dieu, G. De Cremer, S. Leyre, P. Hanselaer, W. Fyen, B. Sels, and J. Hofkens, *J. Phys. Chem. C*, 2013, **117**, 6998–7004.