1. QD synthesis

Chemicals: Diethylzinc (min. 95%), selenium (Se; 99.99%) and tri-n-octylphosphine (TOP; min. 97%) were purchased from Strem Chemicals. Oleylamine (technical grade, 70%), n-octanethiol, oleic acid (technical grade, 90%) were purchased from Sigma Aldrich. 1-Octadecene (ODE; technical grade, 90%) was purchased from Acros Organics. 1-Dodecylphosphonic acid and zinc acetate dihydrate (Zn(OAc)<sub>2</sub>·2H<sub>2</sub>O) were purchased from Alfa Aesar. All the other chemicals including solvents were purchased from Sigma-Aldrich or Acros Organics and used as received.

Preparation of precursors

0.5 M TOP:Se solution: Se (0.592 g, 7.5 mmol) and TOP (15.0 ml) were mixed in a 20-ml vial, which was sealed with a septum. The mixture was degassed under vacuum at 80 °C for 10 min, filled with N<sub>2</sub>, and stirred until Se was dissolved.

0.2 M Zn oleate solution: Zn(OAc)<sub>2</sub>·2H<sub>2</sub>O (2.634 g, 12.0 mmol), oleic acid (7.57 ml, 24 mmol) and ODE (43.8 ml) were loaded into a 100-ml three-neck round bottom flask. The mixture was degassed under vacuum at 100 °C to remove volatiles, filled with N<sub>2</sub>, heated to 230 °C to dissolve the Zn precursor, and cooled to room temperature. After oleylamine (7.90 ml, 24 mmol) was added, the mixture was degassed under vacuum at 100 °C for 30 min and backfilled with N<sub>2</sub>.

0.2 M n-octanethiol solution: n-Octanethiol (0.52 ml, 3.0 mmol) was dissolved in 14.48 ml of ODE.

ZnSe core synthesis

Oleylamine (20 ml) was loaded into a 100-ml four-neck round-bottom flask. The oleylamine solution was degassed under vacuum at 100 °C for 30 min. After filling with N<sub>2</sub>, the solution was heated to 295 °C, and 0.5 M TOP:Se solution (3.0 ml, 1.5 mmol) was slowly injected to the oleylamine solution. 0.5 M ZnEt<sub>2</sub> in TOP (3.75 ml, 1.875 mmol) was swiftly injected at 295 °C with vigorous stirring. The reaction mixture was kept at 290 °C, and aliquots were periodically taken to monitor the core growth by absorption spectroscopy. In order to grow the large core, 0.5 M ZnEt<sub>2</sub> in TOP and 0.5 M TOP:Se were further added dropwise via syringe pump until the lowest absorption band reached the desired wavelength. Afterwards the reaction mixture was allowed to reach room temperature, and then n-butanol (14 ml) was added. The reaction mixture was aliquoted into 40 ml vials. Excess isopropanol and ethanol were added to each vial to flocculate the QDs. The mixtures were centrifuged at 3,800 rpm for 5 min. The supernatant was discarded, and the QD pellets were dissolved in a minimum amount of toluene. This cleaning procedure was repeated an additional time. The QD pellets were dissolved in toluene and stored in the dark until use.

ZnSe/ZnS synthesis

ODE (8.0 ml), oleylamine (6.0 ml), TOP (4.0 ml), 1-dodecylphosphonic acid (17.4 mg, 7.0 × 10<sup>-5</sup> mol) and ZnSe QD core (1.2 × 10<sup>-7</sup> mol in 0.5 ml of toluene) were loaded into a 100-ml four-neck round-bottom flask. The reaction mixture was degassed under vacuum at 100 °C to remove toluene and other volatiles, and
filled with N\textsubscript{2}. The amount of shell precursors required to form 5 monolayers of ZnS was calculated following the literature procedure\textsuperscript{[1]}. 0.2 M Zn oleate solution and 0.2 M \textit{n}-octanethiol solution were added dropwise separately via syringe pump starting at 280 °C, and the reaction mixture was heated to 310 °C during the overcoating process. A 1.5 fold excess of \textit{n}-octanethiol was used compared to Zn oleate. After the precursor addition was completed, the reaction mixture was further annealed at 200 °C for 60 min.

2. TEM Images

![Figure S1](image.jpg)

\textit{Figure S1}: TEM images of ZnSe/ZnS alloy blue emitting QDs. Imaged using a JEOL 2200-FX analytical high-resolution TEM with a 200 kV accelerating voltage. Samples were prepared by spreading a 5–10 \(\mu\)l drop of 0.25 \(\mu\)m filtered QDs (~ 1 \(\mu\)M) onto an ultrathin carbon/holey support film on a 300 mesh Au grid (Ted Pella, Inc.) and air drying. Individual particle sizes were measured using a Gatan Digital Micrograph (Pleasanton, CA); a mean average diameter of 9.7 ± 0.8 nm was extracted from analysis of >100 nanoparticles. Images A) and B) correspond to the same sample at different magnifications.
3. Polymer Synthesis

Scheme S1: Synthesis of PCf: (6-[p-(Aminomethyl)phenyl]-3-[3,3,4,4,5,5-hexafluoro-2-(6-iodo-2-methyl-1-oxo-1-thia-3-indenoyl)-1-cyclopenent-1-yl]-2-methyl-1-thia-1,1-indenedione) 1) $K_2CO_3$, Palladium(II)acetate, THF/EtOH (3:2) vigorous stirring for 30 min at RT. Water is then added dropwise, stopping before a phase separation is observed. RT for 60 additional min. 2) Trifluoroacetic acid in CHCl₃, RT for 60 min.

Scheme S2: Conjugation of PCf to polymer. 1) 66% of dodecylamine, THF (anh.), 55 °C for 3 h. Remaining dodecylamine added, 55 °C for 10 h.
4. NMR Spectra

The NMR spectra of PCf-Boc are presented. The molecule is representative of the amide bond formed with the polymer and demonstrated long-term stability required for $^{13}$C NMR as compared to the free amine PCf.

$^1$H NMR (400 MHz, CDCl$_3$): $d$ 1.26 (9H), 1.85 (0.5H, closed), 2.05 (4H, open, parallel), 2.21 (1.5H, open, anti-parallel), 4.93 (2H, CH$_2$), 6.8 – 8.4 (10H, aromatic). $^{13}$C NMR (CDCl$_3$): $d$ 22.84, 27.06, 29.42, 29.84, 30.33, 31.58, 31.87, 32.07, 53.96, 121.46, 123.76, 127.40, 127.46, 128.06, 128.39, 131.74, 136.15, 136.65, 138.19, 140.03, 140.38, 142.71, 142.93, 156.05.
5. Measurements

Absorbance: Absorbance was measured in a 10×2 mm quartz cuvette with an Agilent 8453 UV-Visible Chemstation.

Fluorescence: Constructs were measured in microtiter 96-well plates (80 µl per well) and fluorescence was collected on a Tecan Infinite M1000 Dual Monochromator Multifunction Microtiter Plate Reader.

Automated irradiation and measurements setup: Samples were irradiated using a Hg arc lamp and band pass filters (340 ± 10 nm, 450 ± 20 nm). A custom built dual absorbance-fluorescence spectrometer with photoconversion capabilities was used to determine spectra and photoconversion (cyclization, cycloreversion) kinetics and quantum yields. Details can be found in Gillanders et. al.[2] Closed 5x5 mm quartz cuvettes with Teflon-coated magnetic stirrers were used and temperature was controlled at 20 ºC for the duration of the experiments. Fluorescence quantum yields were determined relative to Fluorescein in basic solution and Coumarin X in ethanol.

6. Absorbance spectra

![Absorbance spectra](image)

**Figure S3**: Absorbance spectra of the polymer PMA-PCf-C12 [800 nM] and of csQD [133 nM] in open and closed forms.
7. Spectral Overlap

Figure S4: Calculated spectral overlap integral versus wavelength for the QD with the closed and open PCf.

8. Photobleaching

Figure S5: Bleaching of QD fluorescence during an example of cycle measurements. Irradiation during intensity decrease was with UV, 1.4 mW cm⁻², 600 s; Vis, 28.3 mW cm⁻², 1200 s during intensity increase. The final photobleaching values for the QD were obtained by comparing the maximum value to the intensity after the final Vis irradiation; for the PCf they were obtained by comparing the maximum value to the intensity after the final UV irradiation.
9. Kinetic Analysis

The kinetic values were estimated for the PCf conversion within the 3 systems, PCf, PMA-PCf-C12, and the csQD. The first two systems were measured in CHCl$_3$ as solvent and the PCf was assumed to be in a CHCl$_3$ equivalent microenvironment as part of the csQD. We utilized the increase and decrease in fluorescence signal to determine the kinetics, as it was more robust than the absorbance spectra. The photoconversion efficiency decreased as the sample became progressively more complex. The csQD demonstrated much slower apparent PCf conversion. A quantitative treatment of how QDs modify photochromic conversions is given in Díaz et al.[3] We note that when irradiating the csQD colloidal solutions the QD dominates the photon absorbance. This circumstance and the subsequent transfer of energy from the QD to the PCf greatly modifies the observed kinetics.

Table S1. PCf conversion kinetic parameters (first-order rate constants)

<table>
<thead>
<tr>
<th></th>
<th>PCf</th>
<th>PMA-PCf-C12</th>
<th>csQD</th>
</tr>
</thead>
<tbody>
<tr>
<td>Opening$^a$ (ms$^{-1}$)</td>
<td>16</td>
<td>19</td>
<td>2.0</td>
</tr>
<tr>
<td>Closing$^b$ (ms$^{-1}$)</td>
<td>76</td>
<td>32</td>
<td>2.8</td>
</tr>
</tbody>
</table>

[a] 450 nm, 28.3 mW cm$^{-2}$. [b] 340 nm, 1.4 mW cm$^{-2}$

10. Donor-Acceptor Distance Estimates

Due to the large number of PCf distributed around the QD, even with such a small $R_0$ of 2.0 nm the contributions of the open form PCf to the quenching of the QD cannot be assumed a priori to be negligible. Based on the calculated values there were ~155 total PCf per QD. When photoconverting to the closed photostationary state 9 of those PCf converted to the closed form; thus, 146 open form PCf remained. Using Equation S1 (equivalent to Eq. 2 from the main text) we calculate a quenched value for the open csQD, utilizing an initial estimate for $r_{DA}$ of 6.1 nm.

$$E_n = \frac{N\left(\frac{R_0}{r_{DA}}\right)^6}{1+N\left(\frac{R_0}{r_{DA}}\right)^6} \rightarrow \frac{155\left(\frac{2.0}{6.1}\right)^6}{1+155\left(\frac{2.0}{6.1}\right)^6} = 0.16$$

(Equation S1)

It becomes apparent that the observed 33% quenching is in fact additional to an already semi-quenched state. Assigning an emission value of 1.0 to the uncoated QD (no FRET acceptors), the open csQD has an emission of 0.84. The observed 33% quenching is of the 0.84 state, such that the overall FRET efficiency is 0.45. The $r_{DA}$ estimate for the closed form PCf can now be obtained from Equation S2 in which the total FRET efficiency of the closed csQD takes into account the 9 closed PCf as well as the remaining 146 open form PCf ($E_n = 0.153$).
\[ E_n = 0.45 - 0.16 = 0.29 \rightarrow \left( \frac{r_{DA}}{3.7} \right)^6 = \frac{9(1-0.29)}{0.29} \]  
(Equation S2)

The resulting \( r_{DA} \) of 6.2 nm provides a new estimate for the initial open PCf value in Eq. S1. The cycle is iterated until the initial and final estimates of \( r_{DA} \) for the closed PCf converge. The equilibrium value is 6.14 nm, indicating that the open form contribution was negligible within experimental error; we obtain a final estimate of \( r_{DA} \) of 6.1 ± 0.3 nm.

References: