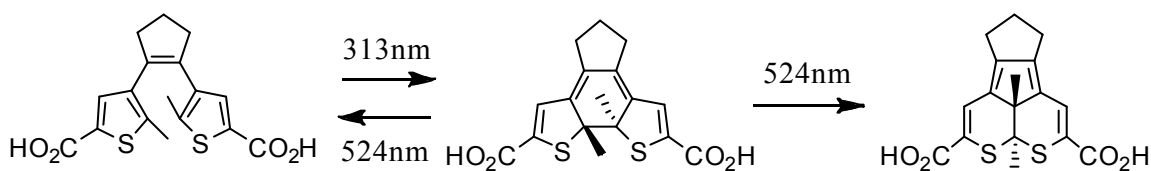


## Supporting Information

### Photocontrol of Luminescent Inorganic Nanocrystals via an Organic Molecular Switch.

Julie Massaad, Yannick Coppel, Michel Sliwa, Myrtil L. Kahn, Christophe Coudret,  
Fabienne Gauffre

#### SI-1: Irreversible isomerization:



Scheme of the irreversible diarylethene isomerization.

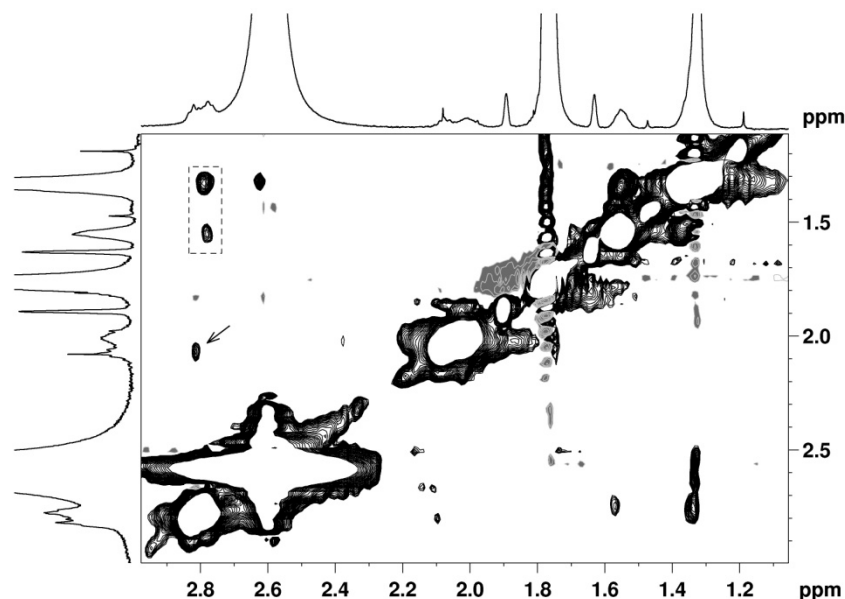
#### SI-2: Comparison of the dye's absolute redox potentials with the ZnO LUMO and HOMO levels

The diacid's first oxidation redox couple of dithienylethene have been measured for both photoisomers: closed form  $E^\circ(\text{DTE-c}^+/\text{DTE-c}) = 0.8 \text{ V vs SCE}$  and open form  $E^\circ(\text{DTE-o}^+/\text{DTE-o}) = 1.4 \text{ V vs SCE}$ .<sup>1</sup> Thus, the closed form is thermodynamically more prone to undergo oxidation than the open one.

compound	$E^\circ_{\text{vs SCE}} (\text{DTE}/\text{DTE}^-)$	$E^\circ_{\text{vs SCE}} (\text{DTE}^+/\text{DTE})$	Level LUMO	Level HOMO	ref
DTE-o	-1.91	+1.4	-2.52 eV	-5.9 eV	2
DTE-c	-	+0.8	-2.3 eV*	-5.2 eV	2
ZnO			-4.35 (VB)	-7.72 (CB)	3
$V_O'$				-6.3eV	4

Table : absolute redox couples of the diacid DTE o/c and levels of ZnO (referenced to vacuum). \* value estimated from the optical gap

### SI-3: NOESY spectra



NOESY (mixing time 100ms) spectra of ZnO Ncs in presence of HDA/DTE-o in a ratio of 2/1. Box highlights the transferred NOE cross-peaks between the  $\alpha$ -CH<sub>2</sub> protons with the other CH<sub>2</sub> protons of HDA. Arrow indicates the transferred NOE cross-peak between the thiophene proton and the closest cyclopentyl proton of DTE-o.

### SI-4: Calculation of the diffusion-controlled bimolecular encounter rate using the Smoluchowski equation

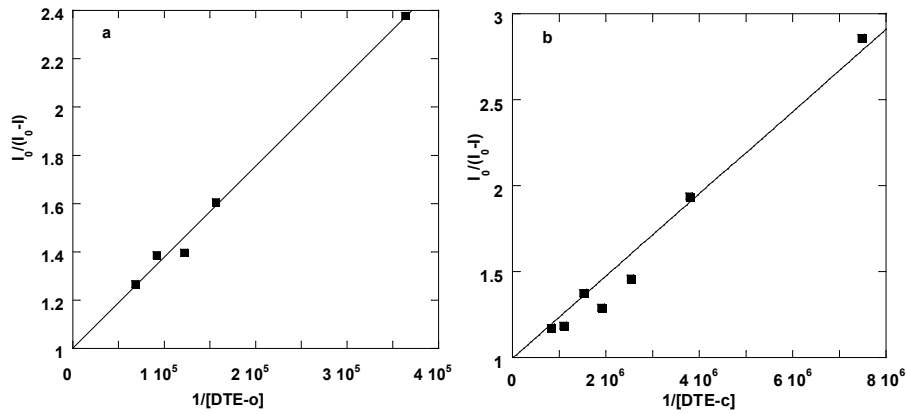
$$k_{\text{diff}} = 4\pi N(R_{Nc} + R_{DTE})(D_{Nc} + D_{DTE})$$

where  $R_{Nc}$  and  $R_{DTE}$ ;  $D_{Nc}$  and  $D_{DTE}$ , stand for the molecular radii and the diffusion coefficients determined by NMR experiments of the Ncs and DTE respectively (expressed in dm and  $\text{dm}^2 \cdot \text{s}^{-1}$  to keep the units correct with the rate constant in  $\text{mol}^{-1} \cdot \text{L} \cdot \text{s}^{-1}$ ). Taking crudely  $R_{Nc} \sim 7\text{nm}$ ;  $R_{DTE} \sim 0.5\text{nm}$ ,  $D_{Nc} \sim 0.7 \times 10^{-10} \text{m}^2 \cdot \text{s}^{-1}$  and  $D_{DTE} \sim 8 \times 10^{-10} \text{m}^2 \cdot \text{s}^{-1}$  we find  $k_{\text{diff}} \sim 5.10^{10} \text{M}^{-1} \cdot \text{s}^{-1}$ .

### SI-5: Determination of the apparent association constant $K_a$ between ZnO and DTE

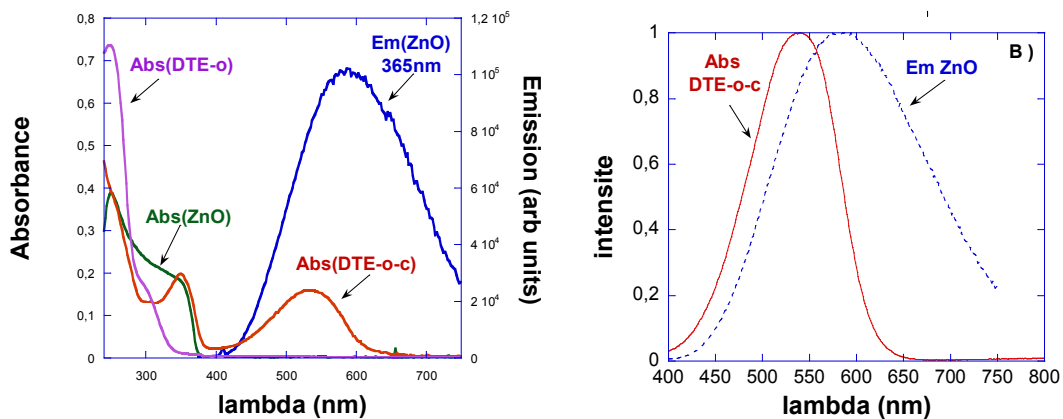
The apparent adsorption constants for DTE-o and DTE-c are determined from the slope of the

best linear fit of  $\frac{I_0}{I_0 - I}$ .  $K_a$  values of  $0.27 \pm 0.02 \cdot 10^6 \text{M}^{-1}$  and  $4.2 \pm 0.2 \cdot 10^6 \text{M}^{-1}$  were found for DTE-o and DTE-c, respectively.



Dependence of  $I_0/(I_0-I)$  on the reciprocal concentration of DTE. (a) Open isomer. (b) Closed isomer after correction for the open isomer.

### SI-6: Förster distance for the DTE-c/ZnO pair



A) UV-vis absorption spectra of THF solutions of DTE-o ( $2 \times 10^{-5}$  M) (purple), of DTE-c-o (red), ZnO Ncs (0.52 mM) (green), and emission spectrum of ZnO Ncs ( $\lambda_{exc} = 365$ nm) (purple). B) Spectral overlap between normalized DTE-c-o absorption- and ZnO-Ncs emission spectra.

The Förster radius ( $R_0$ ) is given by the following relation:

$$R_0 = 0.211 * [\kappa^2 n^{-4} Q_D J]^{1/6}$$

where  $\kappa^2$  is a geometrical parameter describing the relative orientation of the transition dipole moments ( $\kappa^2 = 2/3$  for a random orientation),  $n$  the medium's refractive index,  $Q_D$  the quantum yield of the nanoparticle (energy donor) emission and  $J$ , the overlap integral: <sup>5</sup>

$$J = \frac{\int_0^{\infty} F_D(\lambda) \varepsilon_A \lambda^4 d\lambda}{\int_0^{\infty} F_D(\lambda) d\lambda}$$

With:

$F_D(\lambda)$  : fluorescence intensity of the nanoparticles (dimensionless).

$\varepsilon_A$ : the molar extinction coefficient of the DTE acceptor ( $M^{-1} \text{ cm}^{-1}$ )

We have previously measured  $Q_D = 0.28$  by comparison with quinine sulfate ( $Q_D^{ref} = 0.55$ )

- (1) Massaad, J.; Micheau, J.-C.; Coudret, C.; Sanchez, R.; Guirado, G.; Delbaere, S. *Chemistry* **2012**, *18*, 6568.
- (2) Massaad, J.; Micheau, J.-C.; Coudret, C.; Serpentine, C. L.; Guirado, G. *Chemistry* **2013**, *19*, 12435.
- (3) Kim, H.; Jin, C.; Park, S.; Kwon, Y.; Lee, S.; Lee, C. *Phys. Scr.* **2012**, *T149*, 014052.
- (4) Lima, S.; Sigoli, F.; Jafelicci Jr, M.; Davolos, M. *Int. J. Inorg. Mater.* **2001**, *3*, 749.
- (5) Valeur, B. *Molecular Fluorescence: Principles and Applications*; Wiley-VCH Verlag, W., Ed.; 2001.