Supporting Information

Photo-induced interfacial electron transfer of ZnO nanocrystals to control supramolecular assembly in water

Anna M.Cieślak,† Emma-Rose Janeček,‡ Kamil Sokołowski,† Tomasz Ratajczyk,†

Michał K. Leszczyński,[†] Oren A. Scherman,^{‡,*} and Janusz Lewiński^{†,§,*}

[†] Institute of Physical Chemistry, Polish Academy of Sciences, Kasprzaka 44/52, 01-224 Warsaw, Poland

[‡] Melville Laboratory for Polymer Synthesis, Department of Chemistry, University of Cambridge, Lensfield Road, Cambridge CB2 1EW, United Kingdom

§ Faculty of Chemistry, Warsaw University of Technology, Noakowskiego 3, 00-664 Warsaw, Poland

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1. Materials and methods

All manipulations were conducted under a nitrogen atmosphere by using standard Schlenk techniques. Naphthol-terminated poly(ethylene glycol) (5000 g mol⁻¹) [Np-PEG (2)] was prepared as described previously^[1] as was 1-methyl-4,4'-bipyridinium iodide.^[2] All other reagents were purchased from commercial vendors: 12-bromododecanoic acid (Sigma Aldrich); 2,5,8,11-tetraoxatetradecan-14-oic acid [MeO-dPEG(3)-COOH (ligand B) (Iris Biotech GmbH); diethylzinc (ABCR GmbH); and used as received. The NMR experiments were performed on a Bruker AVANCE II 300 (300 MHz for ¹H NMR; 75 MHz for ¹³C NMR) spectrometer equipped with BBI probe and BVT 3200 variable temperature unit. Powder XRD data were collected on Empyrean diffractometer (PANalytical). Measurements employed Ni-filtered Cu Ka radiation of a copper sealed tube charged with 40 kV voltage and 40 mA current and Bragg Brentano geometry with beam divergence of 1 deg. in the scattering plane. Diffraction patterns were measured in the range of 10-100 degrees of scattering angle by step scanning with step of 0.016 degree. Samples for HRTEM (ZnO NCs 1 and complex 4) were prepared by drop casting of an aqueous solution of the material onto 300-mesh, holey carbon-coated copper grids (Quantifoil). The characterization of size, shape and morphology was carried out on a high resolution Scanning Transmission Electron Microscope (FEI TECNAI G2 F20 S-TWIN) with the following optical parameters: $C_s = 1.2 \text{ mm}$, $C_c = 1.2 \text{ mm}$, electron energy spread = 0.7 eV, beam divergence semi-angle = 1 mrad. Particle size distributions were calculated by counting the diameters of more than 100 particles. Hydrodynamic diameter of NPs was determined by DLS measurements performed on Malvern Zetasizer Nano ZS. Optical absorption spectra for all samples were collected on a Shimadzu UV-2600 spectrophotometer. Photoluminescence measurements were carried out on a RF-6000 Shimadzu Spectrofluorophotometer. The data was analyzed with Origin 8.0, TopSpin 2.1 and MestReNova 11.0.3 software. Herolab UV Hand Lamp (8 Watt) was used as a source of ultraviolet light for exposure of materials. In the all processes described in the manuscript, the source of the oxygen is air.

^[1] Tan, C. S. Y.; del Barrio, J.; Liu, J.; Scherman, O. A. Polym. Chem. 2015, 6, 7652.

^[2] Rauwald, U.; Scherman, O. A. Angew. Chem. Int. Ed. 2008, 47, 3950.

2. Synthesis of 1-methyl-4,4'-bipyridinium-dodecanoic acid bromide iodide $[(MV^{2+}-C_{11}-COOH)\cdot Br\cdot \Gamma);$ ligand A]

12-bromododecanoic acid (1.04 g, 3.6 mmol) and 1-methyl-4,4'-bipyridinium iodide (1.27 g, 4 mmol) were dissolved in acetonitrile (50 ml) and heated to reflux overnight. The resulting precipitate (ligand **A**) was isolated by filtration, washed with cold acetonitrile and then dried under reduced pressure to yield an orange solid (1.3 g, 2.3 mmol, 64%). ¹H NMR (300 MHz; D₂O; 298 K) δ = 9.03 (d, 2H, J = 6.8 Hz), 8.97 (d, 2H, J = 6.8 Hz), 8.45 (dd degenerated to the triplet, 4H, J = 6.2 Hz), 4.64 (t, 2H, J = 7.2 Hz), 4.42 (s, 3H), 2.26 (t, 2H, J = 7.4 Hz), 2.09-1.93 (m, 2H), 1.57-1.41 (m, 2H), 1.36-1.10 (m, 14H) ppm. ¹³C NMR (75 MHz; D₂O; 298 K) δ = 180.4, 150.8, 150.6, 147.1, 146.2, 127.7, 127.4, 63.1, 49.6, 34.7, 31.3, 29.1, 29.1, 29.1, 29.0, 28.9, 28.7, 25.9, 25.1 ppm. HRMS (EI-TOF) *m/z* calcd for C₂₃H₃₄N₂O₂= 370.2620, found 370.2610.

3. Synthesis of water-soluble ZnO NCs functionalized with methyl viologen (MV²⁺) derivatives [ZnO@MV²⁺ NCs (1)]

The water-soluble ZnO@MV²⁺ NCs (1) were prepared by coating the ZnO NCs with carboxylate anchoring moieties linked to either MV²⁺ or a neutral PEG according to the original organometallic synthetic approach.^[3] Precursor solution (S1) was prepared in -78°C by mixing of Et₂Zn (1 mmol, 124 mg) in THF (5 mL) with 2 mL of 1 M water solution in THF. The S1 was then brought from -78°C to -15°C and stirred for 2 hours. The resulting mixture was then warmed up to 25°C and stirred for further 12 hours. After this time: (*i*) 1 mL of the stock solution (THF; 0.15 M) of 2,5,8,11-tetraoxatetradecan-14-oic acid (ligand **B**) and (*ii*) various amounts of 1-methyl-4,4'-bipyridinium-dodecanoic acid bromide iodide (ligand **A**: **a** = 5 wt.%, **b** = 10 wt.% and **c** = 20 wt.%; based on ligand **B**) were added. The resultant mixture was then stirred for further 7 days to produce well dispersed ZnO NCs (samples **Sa-Sc**, respectively). After evaporation of THF, the MV²⁺ functionalized ZnO NCs **Sa-Sc** were readily dispersed into water. The water-solubility and stability as well as organic shell composition of the systems **Sa-Sc** enabled the selection of system **Sb** (ZnO@MV²⁺ NCs; **1**) as the most promising for further application in CB[8] chemistry. The water-solubility, stability, morphology as well as organic shell composition of ZnO NCs **1**

^[3] Cieślak, A. M.; Pavliuk, M. V.; D'Amario, L.; Abdellah, M.; Sokołowski, K.; Rybinska, U.; Fernandes, D. L. A.; Leszczyński, M. K.; Mamedov, F.; El-Zhory, A. M.; Föhlinger, J.; Budinská, A.; Wolska-Pietkiewicz, M.; Hammarström, L.; Lewiński, J.; Sá, J. *Nano Energy* 2016, *30*, 187.

was confirmed by dynamic light scattering (DLS), HRTEM, PXRD, as well as optical measurements (*vide infra*).

4. Characterization of ZnO NCs 1





Figure S1. Absorption and photoluminescence spectra (excitation at 355 nm; 298 K) of ZnO NCs 1 dispersed in water. The ZnO NCs 1 show the characteristic absorption of ZnO semiconductor nanoparticulate materials with a maxima at $\lambda_{max} = 355$ nm. The emission spectra shows a small emission peak at around 388 nm and pronounced emission at 580 nm.

Powder X-Ray diffraction (PXRD)



Figure S2. The PXRD profile of ZnO NCs 1 (*black line*) and simulated ZnO pattern (*red line*). Based on the reflection broadening, according to the Scherrer equation, the crystallite size has been estimated to be 6.0 ± 0.2 nm.

High-Resolution Transmission Electron Microscopy (HRTEM)



Figure S3. The STEM (*a*) and HRTEM (*b*) micrographs of ZnO NCs 1 in water.



Figure S4. Statistical analysis of the size of ZnO NCs 1 based on TEM imaging. Mean size: 7.1 ± 1.1 nm.

Dynamic light scattering (DLS)



Figure S5. The average hydrodynamic diameter (D_h) 9 ± 2 nm of ZnO NCs 1 in water estimated by DLS.



Figure S6. ¹H NMR spectra (300 MHz; D₂O; 298 K) of deuterium water solution of ZnO NCs 1; ligand **A** and ligand **B** (*a-d*). In the ¹H NMR spectrum of ZnO NCs 1 the signals of the ligand **A** at $\delta = 2.08$ ppm and $\delta = 1.45$ ppm attributed to α -CH₂ and β -CH₂ groups, adjacent to anchor carboxylic functionality, are clearly shifted in comparison to the corresponding free ligand **A** ($\delta = 2.26$ ppm and $\delta = 1.49$ ppm, respectively). The signals of the co-ligand **B** at $\delta = 2.47$ ppm and $\delta = 3.69 - 3.73$ ppm attributed to β -CH₂ and α -CH₂ groups, respectively, are clearly shifted in comparison to the corresponding signals from free ligand B ($\delta = 2.61 - 2.65$ ppm and $\delta = 3.74 - 3.78$ ppm). In the FT-IR spectrum of ZnO NCs 1 (*e*) the intensive bands at 1434 and 1564 cm⁻¹ characteristic for carboxylate (O–C–O) stretching modes are observed. This indicates that the ligand **B** as well as ligand **A** are anchored to the ZnO surface in the deprotonated form. Notably, signals of the viologen moiety of ligand A (distanced from anchoring carboxylate group; 8.3-9.1 ppm) remain at the same position after ZnO NCs functionalization. (*-signals from residual tetrahydrofuran).

5. Formation of surface-localized hetero-ternary complexes of $ZnO(a) \{MV^{2+} \cdot Np-PEG \subset CB[8]\}$ (3)

Preparation of complex 3

The molar ratio of functional ligands **A** and **B** of ZnO NCs **1** was estimated by NMR spectroscopy (see Figure S6), hence, the general procedure of preparation of the 1:1:1 ternary complexes can be described as for a ZnO NCs 1/Np-PEG 2/CB[8] 1.0/0.18/0.06 wt.%/wt.%/wt.% composite. ZnO NCs **1** (10 mg) in Milli-Q water (1 mL) was mixed with CB[8] (0.6 mg) followed by addition of 1 equivalent of polymer **2** (1.85 mg).

UV-Vis studies



Figure S7. Absorption spectra (298 K) of ZnO NCs 1 (*solid line*), the mixture of ZnO NCs 1 and polymer 2 (*dashed line*), and complex 3 (*dotted line*) dispersed in water. After the addition of 1 eq. of CB[8] to the mixture of ZnO NCs 1 and polymer 2 new charge-transfer bands appeared indicating charge transfer (CT) type interaction between the electron-deficient MV^{2+} moiety of ZnO NCs 1 and the electron-rich naphthol moiety of polymer 2 forming system 3.

¹H NMR studies



Figure S8. ¹H NMR (300 MHz; D₂O; 298 K) spectra of: (*a*) polymer **2**; (*b*) mixture of ZnO NCs **1** and polymer **2** (MV²⁺:Np moieties ratio 1:1); (*c*) supramolecular nanosystem **3**; and (*d*) the control involving equimolar mixture of ligand **A**, polymer **2** and CB[8]. Upon addition of CB[8] to the mixture of ZnO NCs **1** and polymer **2** (spectrum *c*), signals attributed to viologen moiety (9.1-8.3 ppm) of ZnO NCs **1** as well as naphthalene (8.0-7.3 ppm) moiety of polymer **2** were substantially broadened and shifted, indicating formation of the ZnO@{MV²⁺•Np-PEG⊂CB[8]} (**3**) complex. The inset (*e*) shows broadening of signals attributed to CB[8] protons in system **3** (*bottom spectrum*) in comparison to the analogues conjugate involving CB[8], polymer **2** and molecular ligand **A** (*top spectrum*).





Figure S9. Host-guest complexation of polymer 2 within organic shell of ZnO NCs 1 in the presence of CB[8] monitored by DLS. We note, that upon addition of CB[8] to the mixture of ZnO NCs 1 and polymer 2 we observe only slight increase of the D_h , compared to ZnO NCs 1 alone. This suggests that the PEG chains of 2, assembled within supramolecular system 3, are likely not fully extended away from the ZnO NCs' organic coating, but possibly wrap around individual nanoparticles.



Figure S10. Photoluminescence spectra (excitation at 355 nm; 298 K) of aqueous solutions of: (*a*) ZnO NCs **1** (*straight line*); (*b*) mixture of ZnO NCs **1** and polymer **2** (MV²⁺:Np moieties ratio 1:1; *dashed line*); (*c*) supramolecular nanosystem **3** (*dotted line*).

6. Disassembly of system 3 through the use of a competitive guest, (ferrocenylmethyl)trimethylammonium iodide ($tmaFc^+$)



Figure S11. ¹H NMR (300 MHz, D₂O; 298 K) spectra of: (*a*) supramolecular system **3**; and (*b*) supramolecular system **3** in the presence of tighter binding guest *tma*Fc+. Upon addition of competitive guest the signals attributed to viologen moiety (9.1-8.3 ppm) of ligand **A** within ZnO NCs **1** as well as naphthalene (8.0-7.3 ppm) moiety of polymer **2** are recovered, indicating that *tma*Fc+ is capable of displacing both the MV²⁺ and Np guests with subsequent formation of the *tma*Fc+ \subset CB[8] complex. The inset (*c*) shows that upon formation of *tma*Fc+ \subset CB[8] molecular complex the signals attributed to CB[8] protons became sharp and well resolved (*top spectrum*) in comparison to presented nanoparticulate complex **3** (*bottom spectrum*).



Figure S12. Absorption spectra (298 K) of aqueous solution of: (*a*) nanoparticulate complex **3** (*solid line*) and (*b*) system **3** in the presence of tighter binding guest *tma*Fc+ (*dashed line*).



Figure S13. Photoluminescence (excitation at 355 nm; 298 K) of aqueous solutions of: (*a*) nanoparticulate complex **3** (*solid line*) and (*b*) system **3** in the presence of tighter binding guest tmaFc+ (*dashed line*). The addition of tmaFc+ to an aqueous solution of **3** led to the formation of tmaFc+⊂CB[8] with concomitant release of polymer **2** and regeneration of starting ZnO NC **1** with photo-physical properties intact.



Figure S14. Absorption spectrum of: (*a*) aqueous solution of ZnO NCs **1** (*black line*); (*b*) aqueous solution of ZnO NCs **1** after UV-light irradiation ($\lambda = 366$ nm, 120 min) in the absence of O₂ (*blue line*); and (*c*) the control experiment involving ligand **A** and sodium dithionite Na₂S₂O₄ as a reducing agent (*dashed line*); (*d*) the mixture of ZnO NCs **1** and CB[8] (2:1; based of MV²⁺ content) in water after UV-light irradiation ($\lambda = 366$ nm, 120 min) in the absence of O₂ (*magenta line*). Upon UV-light exposure of ZnO NCs **1** new bands at 400 nm and 600 nm emerged indicating formation of MV⁺⁺ monoradical cations.^[4] The emerging interfacial MV⁺⁺ species can be further utilized for host-guest binding in the presence of CB[8] macrocyles, affording the 2:1 inclusion complexes ZnO@{(MV⁺⁺)₂⊂CB[8]} (**4**) as confirmed by the appearance of new UV-Vis absorption bands at $\lambda = 540$ and 960 nm.^[4]

^[4]Jeon, W. S.; Kim, H.-J.; Lee, C.; Kim, K. Chem. Commun. 2002, 1828.

PL studies



Figure S15. Photoluminescence spectra (excitation at 355 nm; 298 K) of ZnO NCs **1** in water (*blue line*). The emission spectra show that continuous UV-light ($\lambda = 366$ nm, 120 min) irradiation of the semiconducting ZnO NCs **1** in the absence of O₂ led to quenching of the sample visible photoluminescence (*magenta line*).

8. Light-induced redox-coupled release of polymer 2 from supramolecular system 3



Figure S16. Photoluminescence spectra (excitation at 355 nm; 298 K) of mixture of supramolecular nanosystem **3** and ZnO NCs **1** (1:1; based of MV²⁺ content) in water (*blue line*). The emission spectra (*magenta line*) shows that treatment of the presented system with UV light ($\lambda = 366$ nm; 120 min) in the absence of O₂ leads to quenching of the sample visible photoluminescence. Further exposure of this system to O₂ led to recovery of its luminescent properties (*blue dotted line*) with reconstruction of the starting supramolecular system **3** (*vide infra* Figure S21).



Figure S17. Absorption spectrum of the mixture of supramolecular system **3** and ZnO NCs **1** (1:1; based of MV^{2+} content) in water (*solid line*). Treatment of the presented system with UV light ($\lambda = 366$ nm; 120 min) in the absence of O₂ resulted in appearance of new UV-Vis absorption bands at $\lambda = 540$, and 960 nm (*dashed line*), indicating the formation of the homo-ternary 2:1 inclusion complexes within ZnO@{(MV⁺⁺)₂⊂CB[8]} (**4**) system and free polymer **2**.^[3]



Figure S18. DLS measurements of interparticulate assembled system 4 in water; in solution the resulting system 4 consists of two distinct populations of aggregates with D_h of 80 ± 10 nm and 800 ± 100 nm.

HRTEM studies



Figure S19. The HRTEM images of a mixture of ZnO NCs 1 and supramolecular system 3 (1:1; based on MV^{2+}) in water.



Figure S20. Statistical analysis of the complex **4** aggregates size based on TEM imaging. Two populations of aggregates were observed with mean sizes of 413 ± 59 nm and 793 ± 136 nm.

¹H NMR studies



Figure S21. ¹H NMR (300 MHz; D₂O; 298K) spectra of: (*a*) polymer **2**; (*b*) supramolecular system **3**; (c) mixture of supramolecular system **3** and ZnO NCs **1** (1:1 based on MV²⁺), after UV-light ($\lambda = 366$ nm; 120 min) irradiation in the absence of O₂ (*c*') and upon further exposition to O₂ (*c*''). The

¹H NMR spectra showed that UV-light treatment ($\lambda = 366$ nm; 120 min) of the mixture of the system **3** and ZnO NCs **1** led to the appearance of signals corresponding to the naphthalene (8.0-7.3 ppm) moieties of free polymer **2**. Signal of free **2** is most likely broadened due to dynamics and equilibrium between emerging homoternary complexes (MV⁺⁺)₂⊂CB[8] and heteroternary systems MV²⁺•Np-PEG⊂CB[8] as well as presence of paramagnetic species. Additionally, broadening of the ¹H NMR signals attributed to CB[8] protons was observed (*c'*), due to paramagnetic nature of MV⁺⁺ moieties interacting with CB[8] cavity, indicating the formation of 2:1 inclusion complexes **4**. Further exposition of the system to O₂ led to broadening of signals attributed to Np moiety of polymer **2** and recovery of starting supramolecular system **3**. Interestingly, the aromatic signals from free MV²⁺ is much broadened in comparison to spectrum c, which can indicate enhanced dynamics in the system at this stage.