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ARTICLE

Anionic polymerization by electron transfer process from a CdSe quantum dots - perylenediimide (PDI) system

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Reversible physical interactions between CdSe quantum dots (QDs) and perylenediimide (PDI) derivatives have been investigated. Original processes, dependent on the concentration of the two species, contact time, temperature and pH, were observed. The combining of the two solutions resulted in the formation of an electron transfer complex (ETC) due to the transfer of an electron from CdSe nanoparticles to PDI, followed by the formation of the final particularly stable dianion PDI²⁻ species through another electron transfer process. The anionic species was employed for the polymerization initiation of glycidyl methacrylate (GMA). Some aspects of the anionic polymerization mechanism have been investigated.

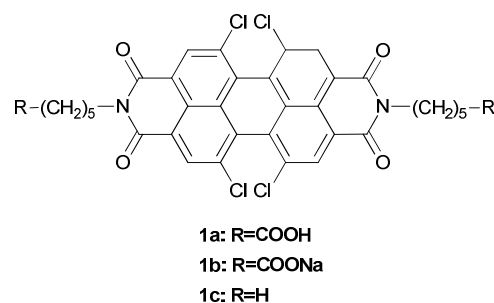
Introduction

As a result of their outstanding optical, thermal and chemical stability as well as redox properties, perylenediimide (PDI) chromophores have found applications in various fields including pigments,¹ optical switches,² logic gates,³ molecular switches or wires,⁴ sensors,⁵ laser dyes,⁶ supramolecular architectures⁷ and organic electronics.⁸

The current research related to colloidal semiconductor QDs has been focused mainly on their utilization either as optical markers in biological systems⁹ or for the properties enhancement of optical materials in applications such as photovoltaic devices.¹⁰ Special attention should be paid to each component energy levels and to the formation of QDs–dye assemblies in order to optimize the controlled processes such as photoinduced charge transfer¹¹ or energy transfer.¹²

Here, we report a reversible electron transfer process between a PDI derivative and CdSe QDs occurring in aqueous media. The mixing of PDI **1a** (Scheme 1) solution in THF with a CdSe water dispersion affords a dramatic change of the solution colour from orange to bright green. This observation could suggest a physicochemical interaction such as an electron transfer process between the two components. Nevertheless, this phenomenon was accompanied by the formation in time (~ after 1 h) of a precipitate resulting from the insolubility of PDI **1a** in aqueous media.

In order to explain the colouring modification process avoiding the formation of a precipitate, the system was revised by using both components in aqueous solutions. Thus, PDI **1a** was transformed into its sodium carboxylate form **1b** using NaOH and the resulting aqueous solution was mixed with the aqueous CdSe dispersion. In this case, the colour modification took place in time, without the precipitate formation.



Scheme 1: Molecular structures of PDI **1a**, PDI **1b** and PDI **1c**. On the contrary to the first experiment carried out using PDI **1a** in THF and CdSe in water, a remarkable reversibility of the colouring change was observed with PDI **1b** and CdSe in water solutions. Under external stimuli (addition of oxygen and stirring, pH decrease), the mixture returns to the initial colour, and the variation process is repeated with a faster formation rate of the green colour compared to the first colour modification (first cycle). The reformation of the green colour corresponds to our second cycle (as presented in the video). The multireversibility of the process constitutes a very important characteristic of the system. (See Electronic supporting information S1 video). Nevertheless, the duration of the colour variation for the next cycles remains constant. Considering that we have observed a time dependent colour variation, the first analysis consisted in the UV-Vis absorption characterization of the initial and final mixtures.

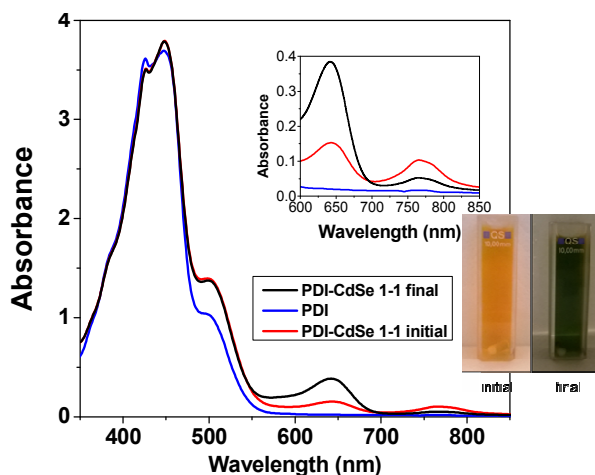


Figure 1: UV-Vis spectra for: PDI **1b** in water (concentration $6.1 \cdot 10^{-4} \text{M}$); initial (2 min) mixture molar ratio PDI-CdSe (1:1); final (1 h) mixture molar ratio PDI-CdSe (1:1); temperature = 25°C

The absorption spectrum of PDI **1b** presents the characteristic bands of the PDI H-aggregates^{13, 14} (Figure 1), which remain constant for the initial and final mixture (450 nm and 500 nm). However, two new bands are observed at 640 nm and 760 nm for the mixture PDI **1b**-CdSe in both cases, but with slightly different intensities (detail in Figure 1).

The evolution in time of the PDI **1b**-CdSe mixture was followed by UV-Vis spectroscopy. Due to its shorter interval, the second cycle was selected for the spectra registration. The second cycle presents the colour modification (orange to green) after interaction with oxygen.

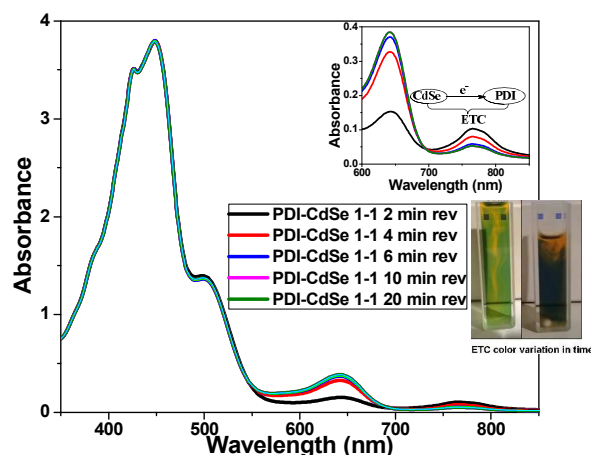
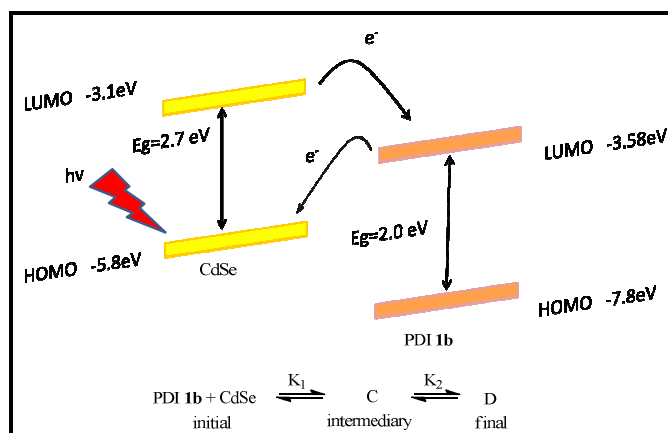


Figure 2: UV-Vis spectra registered during the second cycle for a PDI **1b** (conc. $6.1 \cdot 10^{-4} \text{M}$)-CdSe molar ratio 1:1; temperature = 25°C

In the inset of Figure 2, a severe decrease of the band at 760 nm coupled with the concomitant increase of the band at 640 nm is observed. The reduction of the intensity at 760 nm sustained the formation of an intermediary species, noted C (Scheme 2). Its concentration decreased in time up to consumption, thus confirming its thermodynamic instability. The peak intensity at 640 nm increased in time up to a maximum constant value, which suggests the formation of thermodynamically stable species D specific to the final system. In accordance with these observations, the system evolution could be interpreted as (Scheme 2):



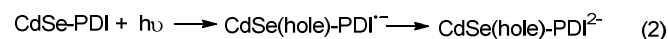
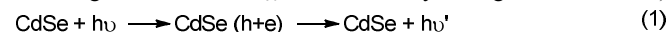
Scheme 2: The physicochemical interaction between PDI **1b** and CdSe quantum dots

The formation rate of the final species D is dependent on the lowest reaction rate, *i.e.* on the formation rate of C and not on the transformation rate of C into D. Therefore, the first step can be considered as the reaction rate determining parameter.

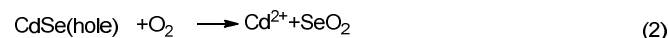
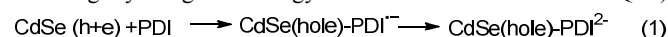
The process description suggested the formation of an electron transfer complex (ETC: PDI^{•-}/CdSe) – C between the electron donor CdSe and the electron acceptor PDI.^{12, 15} The ETC appears to be not stable in time, the system evolving to a more thermodynamically stable species D-(PDI²⁻)¹⁵⁻¹⁸ characterized by the band at 640 nm. The reversible character is due to the electron transfer from the PDI²⁻ to the oxygen present in the solution leading to the neutral PDI.

This electron transfer process is in agreement with the energy levels of both QDs¹⁹⁻²¹ and dye molecules^{22, 23} (see Scheme 2).

We propose two possible mechanisms to explain this process: the first mechanism takes into consideration a photo-induced electron transfer from CdSe to PDI as follows (based on a similar process involving CdSe and C₆₀ described by Bang and Kamat²²):



The second hypothesis is that after electron injection from the CdSe to PDI, in the presence of oxygen - CdSe is oxidised to SeO₂ and the QDs particle size decreases (which does not block the transfer due to the slightly higher energy level of the smaller QDs).



The presence of the PDI²⁻ dianion was confirmed by the pH modification of the mixture after addition of an aqueous HCl solution. This resulted in recovering the orange colour and hindered the reversibility.

The influence on the system behaviour of the molar ratio between the two components was investigated. UV-Vis spectra were recorded during the second cycle for solutions with different molar ratios of PDI **1b**-CdSe. (See ESI Figure S1). The increase of the dilution led to a change in the PDI aggregates formation,^{14, 23} but the system underwent the same transition steps as for the 1:1 ratio. The remarkable aspect was the modification of the peaks intensities at 640 nm and 760 nm which declined with the modification of the molar ratio between the components. This aspect could be explained by the decrease of the reactants concentration and by the formation rate of species C and D, respectively.

For the first cycle, the interval to attain the thermodynamically stable species depends on the molar ratio between the two components. Thus, for an increased molar ratio for the CdSe a faster colour variation was observed.

Considering that the colour variation process is due to a physicochemical interaction involving an equilibrium between several species with different thermodynamic stabilities, the temperature could influence the system evolution. Thus, the mixture PDI-CdSe 1:1 was analysed at two different temperatures, in addition to 25°C.

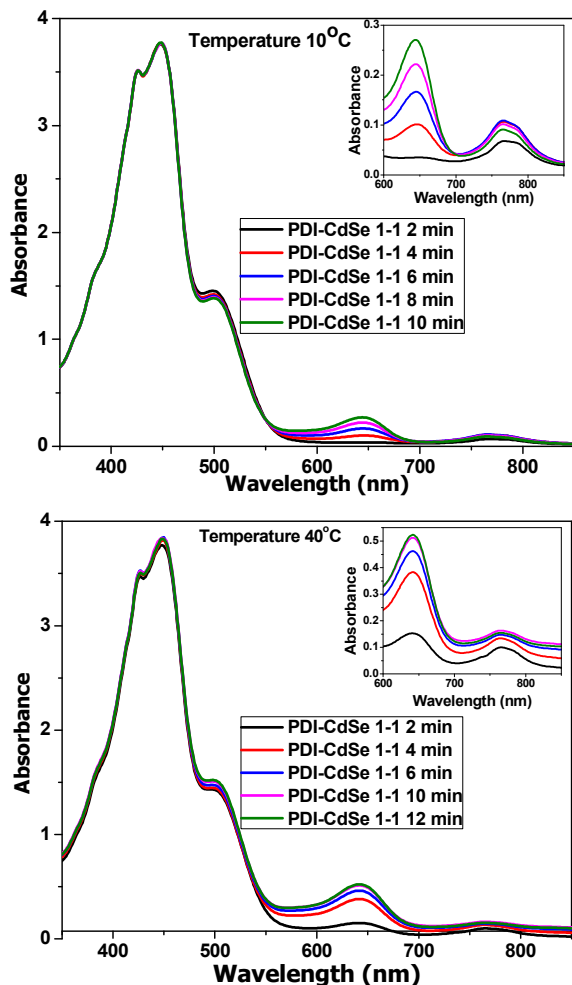


Figure 3: UV-Vis spectra recorded during the second cycle for PDI **1b** (conc. $6.1 \cdot 10^{-4} \text{M}$)-CdSe with 1:1 molar ratio at 10°C (top) and 40°C (bottom)

The comparative analysis between **Figure 2** and **Figure 3** revealed that the concentrations of species **C** and **D** are temperature dependent, since the band intensities increase with the temperature. These observations confirmed that systems **C** and **D** present a characteristic formation rate in accordance with the Arrhenius law. Another observation shows that the species **C** is *thermodynamically metastable* and *kinetically favoured*, whereas the species **D** appears to be *thermodynamically stable*. As both individual components are fluorescent,²⁴ the reversibility process was also analysed for determining the fluorescence modification of the system. In **Figure 4** is presented the evolution of the system emission at an excitation wavelength of 485 nm²⁵, specific for PDI (for PDI **1b**:CdSe 1:2 molar ratio during the reversibility process). The same

behaviour took place for the solutions containing PDI **1b**:CdSe molar ratio 1:1 or 1:4.

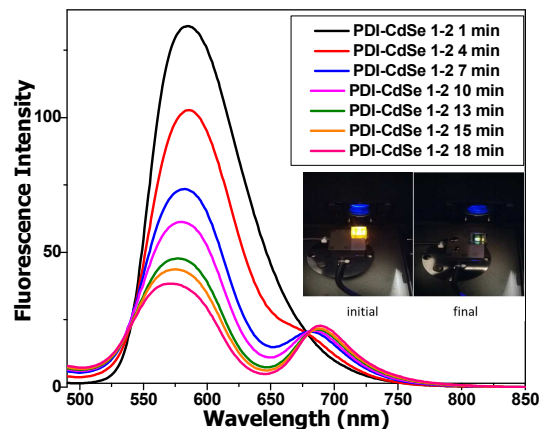


Figure 4: Fluorescence emission spectra during the second cycle for PDI **1b** (conc. $4 \cdot 10^{-4} \text{M}$)-CdSe molar ratio of 1:2 at a temperature of 25°C and an excitation wavelength of 485 nm. The fluorescence emission specific for PDI at 570 nm decreased in time with the formation of another band at 680 nm (**Figure 4**). This behaviour resulted from the formation of species **C** and **D** with the participation of PDI. This phenomenon suggests a partial disruption of the PDI aggregates with the creation of a species presenting a characteristic fluorescence at 680 nm. The intensity of the signal increases with time and is stable enough to confirm the formation of the thermodynamically stable species **D**.

In order to corroborate the presence of PDI²⁻ species, anionic initiated polymerization was realized. For this purpose, the aqueous CdSe quantum dots solution was concentrated under reduced pressure. Toluene was added and then removed under reduced pressure several times in order to completely eliminate water traces. Resulting CdSe QDs were redispersed in dimethyl sulfoxide and PDI **1c** derivative²⁶ was introduced. The expected colour variation characteristic of the PDI dianion formation was observed. The monomer employed for the polymerization was glycidyl methacrylate (GMA), being chosen due to the multitude of polymer analogous reaction possible afterwards^{27, 28}. Thus, the polymerization of GMA (2 mol/L) was realized using an initiator concentration of 10^{-3}mol/L . The reaction temperature was -5°C and the obtained polymer was precipitated in diethyl ether, filtered and dried.

The polymerization kinetics was studied by determination of the conversion evolution vs time **Figure 5**.

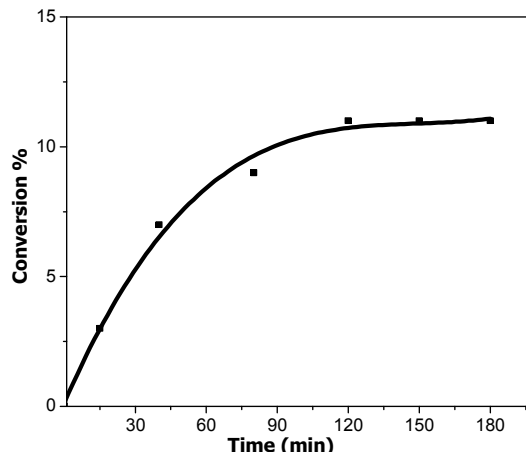


Figure 5. Conversion vs time for GMA polymerization using PDI/CdSe (PDI²⁻) initiator system

The analysis of **Figure 5** reveals that the conversion reaches a limit at around 11%. This maximum is mainly due to the irreversible termination reactions. The value of the conversion is dependent on the initiator concentration and on the k_p/k_t (propagation/termination constants) ratio according to equation (1); a very interesting aspect is the character of the initiation reaction.

$$c = 1 - e^{-\left(\frac{k_p}{k_t}\right)[I]_0} \quad (1)^{29}$$

The GPC analysis was performed for the polymer samples collected at each conversion interval in order to better understand the mechanism. The results are presented in Table 1.

Table 1. GPC data for polymer samples at different conversion values

Time (min)	Conv. (%)	Mn (g/mol)	PDI
15	3.3	71299	1.23
		805	1.02
40	7.1	61144	1.38
		803	1.04
80	9.2	37059	1.40
		800	1.06
120	11.0	21263	1.56
		788	1.05

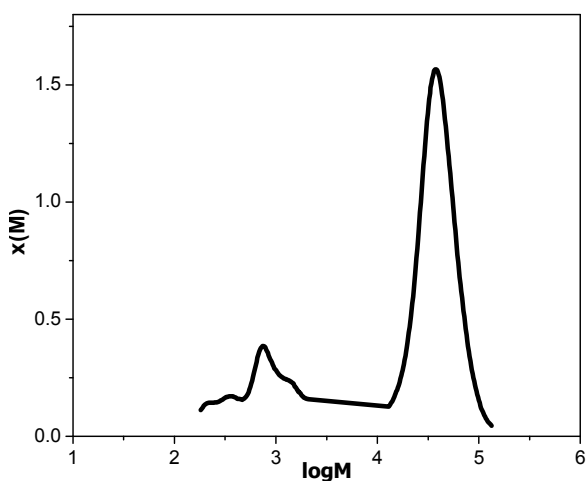
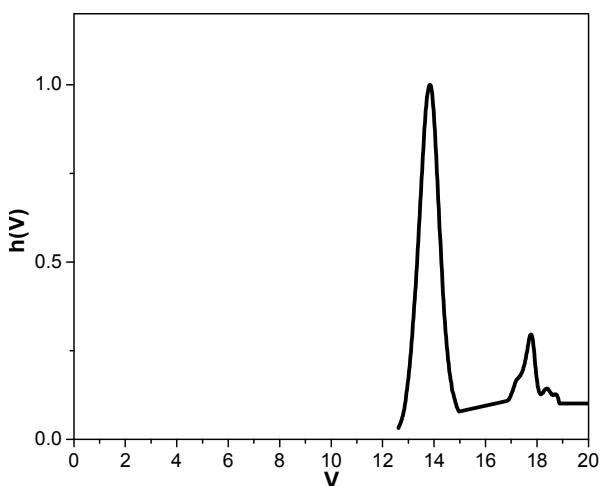


Figure 6. GPC trace analysis at 40 min reaction time processed according to Gavrilov et al.³⁰

In the GPC trace analysis of the polymer samples an interesting peak is present at 780 g/mol. This value can be correlated with the PDI derivative molecular weight, which sustains the lack of chemical grafting of the PDI to the polymer chain. Thus, the initiation is realized through an electron transfer process, followed by the return of the dye to its neutral state. This aspect is noticeable during the experiment, because after the initiator introduction, the solution changes colour from green to orange confirming the electron transfer process.

The value of the molecular weight is directly proportional to the concentration of the monomer and decreases with the reaction time. The variation of the polydispersity index can be explained by a variation of the initiation rate. Thus, a rapid initiation rate is registered in the first stage of the reaction followed by a slow initiation. This slow initiation can be explained by the ability of the PDI/CdSe system to reform the dianion species after the electron transfer process. Consequently, the anionic polymerization of GMA with irreversible termination was realized through initiation using PDI²⁻ species present in a PDI/CdSe system. A more detailed study of the anionic polymerization will be presented in a future study.

Conclusions

We have obtained a reversible electron transfer system involving a PDI derivative and CdSe QDs. The reversibility is due to the partial disruption of the PDI-CdSe aggregates and the electron transfer process from the PDI²⁻ to another acceptor (oxygen). The observed phenomena could find application in the development of oxygen sensors (presenting the advantage of utilizing only a simple colour modification process compared to electrochemical alternatives) or it could be exploited for the realization of solar cells.

Furthermore, we have demonstrated the possibility to initiate anionic polymerization using the PDI dianion species for GMA. Using the GPC analyses some kinetics and mechanism aspects have been highlighted.

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Notes and references

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Electronic Supplementary Information (ESI) available: including experimental procedures, UV-Vis molar ratio influence, TEM QDs, a movie of the reversible process in the presence of oxygen and stability vs nitrogen. See DOI: 10.1039/b000000x/

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