

Article

Photoinduced electron-transfer quenching of luminescent silicon nanocrystals as a way to estimate the position of the conduction and valence bands by Marcus theory

Antonino Arrigo, Raffaello Mazzaro, Francesco Romano, Giacomo Bergamini, and Paola Ceroni *Chem. Mater.*, Just Accepted Manuscript • DOI: 10.1021/acs.chemmater.6b02880 • Publication Date (Web): 02 Sep 2016 Downloaded from http://pubs.acs.org on September 4, 2016

Just Accepted

"Just Accepted" manuscripts have been peer-reviewed and accepted for publication. They are posted online prior to technical editing, formatting for publication and author proofing. The American Chemical Society provides "Just Accepted" as a free service to the research community to expedite the dissemination of scientific material as soon as possible after acceptance. "Just Accepted" manuscripts appear in full in PDF format accompanied by an HTML abstract. "Just Accepted" manuscripts have been fully peer reviewed, but should not be considered the official version of record. They are accessible to all readers and citable by the Digital Object Identifier (DOI®). "Just Accepted" is an optional service offered to authors. Therefore, the "Just Accepted" Web site may not include all articles that will be published in the journal. After a manuscript is technically edited and formatted, it will be removed from the "Just Accepted" Web site and published as an ASAP article. Note that technical editing may introduce minor changes to the manuscript text and/or graphics which could affect content, and all legal disclaimers and ethical guidelines that apply to the journal pertain. ACS cannot be held responsible for errors or consequences arising from the use of information contained in these "Just Accepted" manuscripts.



Chemistry of Materials is published by the American Chemical Society. 1155 Sixteenth Street N.W., Washington, DC 20036

Published by American Chemical Society. Copyright © American Chemical Society. However, no copyright claim is made to original U.S. Government works, or works produced by employees of any Commonwealth realm Crown government in the course of their duties.

Photoinduced electron-transfer quenching of luminescent silicon nanocrystals as a way to estimate the position of the conduction and valence bands by Marcus theory

Antonino Arrigo^a, Raffaello Mazzaro^{a, b}, Francesco Romano^a, Giacomo Bergamini^a, Paola Ceroni^a * ^a Department of Chemistry "Giacomo Ciamician", University of Bologna, via Selmi 2, 40126 Bologna, Italy, e-mail:

paola.ceroni@unibo.it

^b CNR-IMM, Area della Ricerca Bologna, Via Piero Gobetti 101, 40129, Bologna, Italy

KEYWORDS: quantum dot, luminescence, non-adiabatic electron transfer, band gap.

ABSTRACT: Photoluminescence of silicon nanocrystals (SiNCs) in the presence of a series of quinone electron acceptors and ferrocene electron donors is quenched by oxidative and reductive electron transfer dynamic processes, respectively. The rate of these processes is investigated as a function of: (a) the thermodynamic driving force of the reaction, by changing the reduction potentials of the acceptor or donor molecules, (b) the dimension of SiNCs (diameter = 3.2 or 5.0 nm), (c) the surface capping layer on SiNCs (dodecyl or ethylbenzene groups), and (d) the solvent polarity (toluene vs dichloromethane). The results were interpreted within the classical Marcus theory, enabling us to estimate the position of the valence and conduction bands, as well as the reorganization energy (particularly small, as expected for quantum dots) and electronic transmission coefficients. The last parameter is in the range $10^{-5} - 10^{-6}$, demonstrating the non-adiabaticity of the process, and it decreases upon increasing the SiNC dimensions: this result is in line with a larger number of excitons generated in the inner silicon core for larger SiNCs and thus resulting in a lower electronic coupling with the quencher molecules.

Introduction

In the last decades, semiconductor nanocrystals (i.e. quantum dots QDs) have attracted much attention as luminescent materials in bioimaging and display technology and as photoinduced charge separation systems in solar energy conversion and photodetectors.^{1, 2} In this context, the efficiency of the electron transfer processes, detrimental for luminescent materials and desirable for the second field of application, is a key parameter. It is thus crucial to understand the dependence of the rate of electron transfer processes on QD properties in order to improve the efficiency of QD-based devices. These aspects have not been addressed in detail, compared to the large body of work performed on electron transfer between molecules. At a molecular level, the Marcus theory ^{3, 4, 5} predicts the rate of electron transfer to be a function of the thermodynamic driving force (with a normal and inverted region), nuclear parameters related to reorganization energy of the molecules and surrounding solvents to accommodate the change in charge distribution, and electronic factors, as the transmission coefficient that discriminates between an adiabatic (very fast electron transfers) and a non-adiabatic regime.

In this context, luminescent QDs, as CdTe, CdSe, or CdSe/CdS core/shell, functionalized at the surface with molecular acceptor or donor groups were involved in photoinduced electron transfer processes.^{6, 7, 8, 9, 10, 11} The electrontransfer rate constants generally increase by decreasing the QD size: this has been rationalized by the increase of the driving force because of the higher optical band gap for smaller QDs, but the Marcus inverted region has never been observed. The se results have been recently rationalized on the basis of an Auger-assisted mechanism:⁶ the transfer of the electron to the molecular acceptor on the QD surface is coupled to the excitation of the hole, so that the excess energy of the electron promotes hole excitation, overcoming the Marcus inverted region. However, uncertainties are still present since a change of QD size brings about not only a change in the driving force, but also of the reorganization energy and, most importantly, of the electronic transmission coefficient: corrections for these parameters are extremely difficult, if not impossible. Furthermore, a careful estimation of the number of molecular quenchers present at the QD surface is difficult ⁷ and, if not properly addressed, it may cause discrepancies in the series of the reported results.

Within the plethora of luminescent QDs, silicon nanocrystals (SiNCs) are attracting attention in the last few years ¹² for applications ranging from luminescent probes, to sensors and solar cells. ^{13, 14, 15} However, very little attention has been devoted to the study of photoinduced electron transfer processes involving SiNCs as electron donors or electron acceptors. Recently, the luminescence quenching of SiNCs by nitroaromatic compounds (nitrotoulene derivatives, even TNT, among the others) was attributed to a photoinduced charge separation process, ¹⁶ as previously reported also for porous silicon nanostructures.

A study of the parameters which affect the rate of electron transfers involving SiNCs is interesting also to estimate the position of the edges of the valence (VB) and conduction band (CB). Indeed, the band gap can be easily determined by lumi-

ACS Paragon Plus Environment

nescence measurements,^{18, 19} by electrochemiluminescence ²⁰, ²¹ or by scanning tunneling spectroscopy,²² but the position of VB and CB is very difficult to determine since electrochemical measurements on SiNCs does not provide significant signals and only very few reports on the electrochemistry of SiNCs are present in the literature.^{20, 21}

In the present work, we propose dynamic quenching of SiNC luminescence by two series of electron acceptors and electron donors as a viable alternative to locate the position of VB and CB within the Marcus theory. We investigated the electron transfer rate constants as a function of the size of the nanocrystals, either 3 or 5 nm in diameter, the surface functionalization (dodecyl or ethylbenzene groups) and the solvent polarity (toluene vs dichloromethane). Quinones and ferrocene derivatives were selected as electron donors and acceptors, respectively, because of their accessible reduction potentials, which can be tuned over a large range, as well as their wellknown photophysical and electrochemical properties.^{23,24}

To the best of our knowledge, this is the first example in which photoinduced electron transfer processes involving SiNCs are rationalized within the Marcus theory, thus allowing to estimate not only the thermodynamic driving force of the reaction and thus the position of VB and CB (knowing the optical band gap and the reduction potentials of the quenchers), but also the reorganization energy and electronic transmission coefficients.

Results and discussion

Synthesis and characterization of SiNCs

The synthesis of SiNCs (Scheme 1) was performed by thermal disproportionation of hydrogen silsesquioxane, prepared following a literature procedure.^{25, 26} Etching of the silica matrix yielded hydride terminated SiNCs that were functionalized by either a thermal hydrosilylation reaction with 1-dodecene (Scheme 1a) or a photochemical hydrosilylation reaction with styrene (Scheme 1b).^{27, 28} Further details are reported in the Supporting Information.



Scheme 1. Schematic representation of the synthetic strategy adopted to prepare silicon nanocrystals passivated with dodecyl (a) or ethylbenzene groups (b).

The size distribution of two families of nanocrystals with average diameter of 3.2 ± 1.1 nm and 5.0 ± 1.2 nm was analyzed by transmission electron microscopy (TEM), as displayed in Figure 1.



Figure 1. TEM images of SiNCs with diameter of 3.2 ± 1.1 nm (a) and 5.0 ± 1.2 nm (b) and relative HR-TEM magnification showing for both samples the typical Si lattice fringes (c,d). The histogram in the inset shows the average Si core diameter of the nanocrystals.

SiNCs capped by dodecyl or ethyl-benzene groups present the same photophysical properties, demonstrating that the surface layer does not affect their optical features: an unstructured absorption profile, due to the indirect band gap nature of silicon, and an emission in the red or near infrared (NIR) spectral region for SiNCs of 3.2 or 5.0 nm diameter, respectively (see Figure S1). The emission energy is in agreement with the expected trend for quantum confinement in crystalline silicon^{29,30} and the values of emission quantum yields and lifetimes are similar to those previously reported by some of us.^{18,31,32} The most relevant photophysical parameters are reported in Table 1 for dodecyl-capped SiNCs.

Table 1. Luminescence band maximum, emission quantum yield and lifetime of SiNCs with average diameter of 3.2 and 5.0 nm, passivated with dodecyl groups, in air-equilibrated toluene solution.

SiNCs / diameter	$\lambda_{em}/$ nm	$\Phi_{ m em}$	$\tau/\mu s$
3.2 nm	765	0.35	70
5.0 nm	955	0.45	570

Luminescence quenching of 3.2 nm size SiNCs by quinines

A series of quinones, presenting different reduction potentials (Scheme 2 and Table 2), were added to air-equilibrated toluene dispersions of SiNCs (average diameter = 3.2 nm) passiv-

ated by dodecyl chains (concentration of SiNCs ca. 3×10^{-6} M and 8×10^{-7} M for 3.2 and 5.0 nm SiNCs, respectively). The investigated quinones are: 1,4-benzoquinone (**BQ**), chloranil (or tetrachloro-1,4-benzoquinone) (**Cl**₄-**BQ**), 2,5-dichloro-benzoquinone (**Cl**₂-**BQ**), 2,6-dimethyl-benzoquinone (**Me**₂-**BQ**), 1,4-naphtoquinone (**NQ**), 2,3-Dichloro-1,4-naphthoquinone (**Cl**₂-**NQ**), menadione (or 2-methyl naphtoquinone) (**Me-NQ**), 9,10-antraquinone (**AQ**).



Scheme 2. Molecular structure of the investigated quinones.

The absorption spectrum is the mere superposition of the spectra of SiNCs and the quinone (see e.g. Figure S3 for AQ): this indicates that the interaction between the two species is negligible at the ground state. On the other hand, upon excitation at 450 nm (where SiNCs absorb light) a quenching of the SiNC luminescence is observed without any change in the shape of the emission band (Figure 2a). A concomitant decrease of lifetime is registered (Figure S4a), according to the Stern-Volmer equation (Figure 2b): ³³

$$\tau^{0} / \tau = \Phi^{0} / \Phi = 1 + k_{q} \tau^{0} [Q]$$

where τ^0 and τ are the lifetimes of excited SiNC (hereafter named *SiNC) in the absence and in the presence of quencher, respectively; Φ^0 and Φ are the luminescence quantum yield of SiNCs in the absence and in the presence of quencher, respectively; [Q] is the molar concentration of the quencher in solution; k_q is the quenching constant.

(1)



Figure 2. Luminescence quenching of SiNCs (uncorrected spectra) with diameter of 3.2 nm (a) or 5.0 nm (c) by addition of BQ in air-equilibrated toluene ($\lambda_{ex} = 450$ nm). Stern-Volmer plot (eq.

1) reporting the luminescence quantum yields of 3.2 nm (b) and 5.0 nm (d) SiNCs vs the concentration of the quencher **BQ**.

For all the investigated quinones, the plots of Φ^0/Φ or τ^0/τ versus the quencher concentrations are superimposed (see e.g. Figure S4b), demonstrating that the quenching is occurring by a dynamic process. The corresponding k_q values, evaluated by eq. 1, are collected in Table 2.

Table 2. Reduction potentials of the quenchers in dichloromethane solution ($E_{1/2}$ in V vs SCE). Rate constants of the quenching of SiNCs of 3.2 nm and 5.0 nm diameter upon addition of quinones in toluene. In the case of SiNCs of 3.2 nm diameter, the rate constants are reported also in dichloromethane for some selected quinones.

		SiNCs (3.2 nm)		SiNCs (5.0 nm)	
	DCM	DCM	Toluene	Toluene	
Quencher	E _{1/2} / V (vs SCE)	$\frac{k_q}{10^8} \frac{M^{-1}}{M^{-1}} \frac{s^{-1}}{s^{-1}}$	$\frac{k_q}{10^8} \frac{M^{-1}}{M^{-1}}$	$\frac{k_q}{10^8} \frac{M^{-1}}{M^{-1}}$	
Cl ₄ -BQ	- 0.05		8.4	1.15	
Cl ₂ -BQ	- 0.13		10.3	1.37	
Cl ₂ -NQ	- 0.38		11.4	1.40	
BQ	- 0.45	14.0	11.0	1.06	
Me ₂ -BQ	- 0.62		8.0	1.01	
NQ	- 0.69	13.0	6.8	0.61	
Me-NQ	- 0.73		4.9	0.42	
AQ	- 0.88	10.5	1.5	0.34	

Quenching constants larger than $10^7 \text{ M}^{-1} \text{ s}^{-1}$, as in the present case, are generally attributed either to energy or electron transfer processes.³⁴ In the present case, energy transfer from excited SiNCs to quinones can be ruled out, as the excited state of the quinone lies at much higher energy compared to SiNCs (and the emission spectrum of SiNCs does not overlap with the absorption band of the quinone). Furthermore, light excitation of the SiNCs dispersion in the presence of quinones does not lead to changes of the absorption spectrum, ruling out the possibility of a photochemical degradation of SiNCs (see Supporting Information for more details). Therefore, the quenching mechanism can be ascribed to an oxidative electron transfer process, as depicted in Scheme 3.

* SiNCs + Q
$$\stackrel{k_d}{\longrightarrow}$$
 * SiNCs Q
SiNCs⁺ + Q⁻ $\stackrel{k'_d}{\longrightarrow}$ SiNCs⁺ Q⁻

Scheme 3. Schematic representation of the oxidative electron transfer process between SiNCs and quinones.

We can rationalize the experimental k_q values within the Marcus model for electron transfer reactions. ^{3, 35, 4} Figure 3a represents log k_q versus the reduction energy of the quinones E_{red} . **ACS Paragon Plus Environment**



Figure 3. Plot and corresponding fitting curve of quenching constants k_q vs the reduction potential of quinones (in V vs SCE) for the case of 3.2 nm (a) and 5.0 nm (b) SiNCs, in the oxidative electron transfer processes.

As previously reported for photoinduced dynamic electron transfer processes, $^{34, 36, 37, 38}$ the quenching constant k_q can be rationalized on the basis of Scheme 3 and it can be expressed by the following equation:

$$k_{q} = \frac{k_{d}}{1 + \frac{k_{-d}}{k_{e}} + \frac{k_{-d}}{k'_{-d}} \frac{k_{-e}}{k_{e}}}$$
(2)

where k_d is the diffusion rate constant, k_{-d} and k'_{-d} are the rate constants for dissociation of the precursor and successor complex (for more details see Supporting Information), and k_e and k_{-e} are unimolecular rate constants for forward and backward electron transfer processes, respectively.

$$\frac{k_{-e}}{k_{e}} = e^{(\Delta G/RT)} \tag{3}$$

where ΔG is the free-energy change of the electron transfer step and it is related to the reduction potentials of SiNCs and quinones Q by:

$$\Delta G = F[E(SiNC^+ / SiNC) - E_{oo}(*SiNC / SiNC) - E(Q/Q^-)] + w$$
(4)

where F is Faraday constant, E_{00} (*SiNC/SiNC) is the oneelectron potential corresponding to the optical band gap of SiNCs and w is the electrostatic work term that accounts for Coulomb interactions between the partners after electron transfer. #

In the classical Marcus approach, ${}^{3, 35, 4}$ k_e can be expressed by:

$$k_e = \mathbf{k} \, \mathbf{v}_{\rm n} \, \exp(-\Delta \mathbf{G}^* / \mathrm{RT}) \tag{5}$$

where k is the electronic transmission coefficient, v_n is the nuclear factor and ΔG^* is the free activation energy.

$$\Delta G^* = \Delta G + \frac{\Delta G^*(0)}{\ln 2} \ln \left(1 + \exp \left(-\frac{\Delta G \ln 2}{\Delta G^*(0)} \right) \right) \tag{6}$$

where $\Delta G^*(0)$ is the intrinsic barrier (see also Figure S6 in the Supporting Information), a parameter related to the amount of distortion of both the inner coordinates and the outer solvation shells accompanying electron transfer.

If we consider, as in the present case, a series of homogeneous electron-transfer reactions in the same solvent between the same reductant and a series of structurally related oxidants that have variable redox potentials, but very similar size, shape, electronic structure and electric charge, we may assume that throughout the series the reaction parameters k_d, k_{-d} and k'_{-d} in eq. 2, k in eq. 5 and $\Delta G^*(0)$ in eq. 6 are constant. Under these assumptions, k_{α} is only a function of ΔG , i.e. of the redox potentials of the reaction partners (eq. 4). Based on the previously reported equations, a plot of log k_q vs E_{RED} consists of three regions: (i) a plateau region for highly exoergonic reaction, in which k_q is controlled by diffusion and, in case of a nonadiabatic process, by the electronic transmission coefficient k, (ii) an Arrhenius type linear region for endoergonic reactions, and (iii) an intermediate region in which k_a increases in a monotonous way as ERED becomes less negative. Indeed, the experimental data reported in Figure 3a presents this trend. From the best fitting of the data reported in Figure 3a, three parameters are obtained: E(SiNC⁺/*SiNC), $\Delta G^*(0)$ and the product kv_n . The value of E(SiNC⁺/*SiNC) results – 0.87 V, and, estimating E₀₀(*SiNC/SiNC) from the maximum of the corrected emission band (1.62 eV), E(SiNC⁺/SiNC) is + 0.75 V vs SCE. $\Delta G^*(0)$ is 6.5 x 10⁻² eV, a very small value consistent with a low reorganization energy of the apolar solvent and an extremely small inner reorganization energy. Indeed, inner reorganization energy of tens of millielectronvolts have been previously reported for QDs. ^{11, 39} The electronic transmission coefficient k is estimated as 10^{-5} (see Supporting Information for more details), typical for a non-adiabatic process. Therefore, the plateau value of Figure 3a is lower than expected for diffusion-controlled processes since the electron transfer process is non-adiabatic because of the poor electronic coupling of the two partners.

To have a better insight on the role of the surface layer in determining the electron transfer rate and the electronic transmission coefficient \mathbf{k} , we repeated the same experiments for 3.2 nm SiNCs, functionalized with ethyl-benzene groups on the surface, using **BQ**, **NQ** and **AQ** as representative quenchers. No significant difference was evidenced. This is an indication that the dodecyl layer, much thicker than the ethylbenzene one, does not represent a barrier for electron transfer. The quenchers are likely to penetrate within the dodecyl layer, without affecting the SiNC bandgap (no shift of the emission band is observed upon addition of large amount of quenchers both for dodecyl and ethyl-benzene functionalized samples). The non-adiabaticity of the electron transfer is related not to 1

2

3

4

5

6

7

8

9

10

11

12

13

14

15

16

17

18

19

20

21

22

23

24

25

26

27

28

29

30

31

32

33

34 35

36

37 38

39

40

41

42

43

44

45

46

47

48

49

50

51

52

53

54

55

56

57

58

59

60

the insulating barrier created by the surface layer, but to the fact that the luminescence derives from excitons which can be generated inside the nanocrystal, and not from a surface state. Therefore, we expect a distribution of quenching rate constants: higher for excitons located close to the surface and lower for inner ones. Moreover, based on this picture, a lower electronic transmission coefficient is expected for 5.0 nm SiNCs, in which the probability to have an exciton located in the inner part of the nanocrystal is higher compared to the 3.2 nm SiNCs (see discussion below).

It is well-known that the solvent plays a crucial role in charge separation processes, 40 thus we investigated the quenching between SiNCs of 3.2 nm and BQ, NQ and AQ in airequilibrated dichloromethane (DCM) solution (Table 2). As observed for the experiments performed in toluene, the quenching rate constants decrease in the order BQ, NQ and AQ, according to the driving force for the electron transfer. The rate constants k_q are higher in DCM than in toluene in the presence of the same quencher. The solvent affects the following parameters: (i) the free-energy change ΔG (eq. 4) becomes more negative since DCM is more polar (dielectric constant ε = 9.1) than toluene (constant ε = 2.4) and stabilizes charged products; (ii) the diffusion rate constants increase because of the lower viscosity of DCM compared to toluene, and (iii) the solvent reorganization energy (included in $\Delta G^*(0)$) increases. Since the first two parameters bring about an increase of k_a, while the last yields a decrease of k_q values, the first two parameters are determining in the present case, compared to the solvent reorganization energy. In particular, the first term is expected to be the most important one since the increase of diffusion rate constants is limited: for example, k_d increases by ca. 1.4 times.

Luminescence quenching of 5.0 nm size SiNCs by quinones

To verify the correlation between diameter of nanocrystals and electron transfer processes, the same experiments were performed for SiNCs with average diameter of 5.0 nm. Addition of the quinones lead to luminescence quenching and lifetime decrease according to equation 1 (Figure 2d and Table 2), demonstrating the occurrence of a dynamic quenching process. The quenching is attributed to an oxidative photoinduced electron transfer from the excited SiNCs to the guinone since energy transfer is ruled out from a thermodynamic point of view. It is worth noting that, in this case, the quenching rate constants are smaller than in the case of 3.2 nm SiNCs (Table 2). In order to explain such a result, it is useful to discuss the parameters obtained by fitting the curve reported in Figure 3b, as described above. The electronic transmission coefficient k is ca. 10^{-6} , $\Delta G^{*}(0)$ is 4.3 x 10^{-2} eV, and the E(SiNC⁺/*SiNC) is – 0.76 V vs SCE and E(SiNC⁺/SiNC) results + 0.54 V vs SCE, taking E_{00} from the maximum of the emission band: 1.30 eV.

The lower values of k_q for 5.0 nm SiNCs compared to 3.2 nm SiNCs is rationalized by the following considerations: (i) the free energy change ΔG (see Table S1) is lower for 5.0 nm SiNCs, related to the lower energy of the band gap, and (ii) the electronic transmission coefficient *k* is one order of magnitude lower compared to 3.2 nm SiNCs, as in larger nanocrystals the number of inner excitons, more distant from the quinone quenchers, is higher than in smaller ones.

Luminescence quenching of SiNCs by ferrocene derivatives

The same experiments were repeated with electron donor molecule, i.e. ferrocene derivatives: ferrocene (Fc), 1,1'-dimethylferrocence (Me₂-Fc), decamethyl-ferrocene (Me₁₀-Fc). As before, the absorption spectrum in air-equilibrated toluene was the superposition of the spectra of SiNCs and the ferrocenes, indicating that the interaction between the two species is negligible at the ground state. By adding ferrocenes (in large excess) to a solution of SiNCs the luminescence was guenched and the lifetime decreased with an increase of the guencher concentration. In our experiments, excitation was performed at 450 nm in the case of Me₂-Fc and Me₁₀-Fc, and 380 nm in the case of Fc, in order to excite mainly SiNCs. However, a small contribution due to the absorbance of the ferrocenes cannot be excluded, therefore, the k_a values reported in Table 3 are obtained by plotting τ^0/τ versus the quencher concentration since these values are not affected by the percentage of light absorbed by SiNCs or ferrocene derivatives. Energy transfer can be ruled out as a possible quenching mechanism, since ferrocene has a triplet excited state which lies at 1.78 eV, ⁴¹ while the exciton of SiNCs lies at lower energy (ca. 1.6 eV for 3.2) nm and ca. 1.3 eV for 5.0 nm SiNCs). Therefore, the quenching is attributed to a reductive electron transfer: Me_{10} -Fc is the best quencher, followed by Me₂-Fc and Fc, in accordance with the oxidation potentials (Table 3). To fit the data in a diagram logk_a versus the oxidation energy of the ferrocene derivatives (Figure 4), the same treatment as above was used. In the present case, the free energy change can be estimated by equation 7:

 $\Delta G = F[E(Fc^+/Fc) - E(*SiNC/SiNC^-) + E_{oo}(*SiNC/SiNC)] + w$ (7)



Figure 4. Chemical structures of ferrocene derivatives used as electron donor (top). Plot and corresponding fitting curve of quenching constants k_q vs the oxidation potential of ferrocene derivatives (E_{OX} in V, vs SCE) for 3.2 nm SiNCs (bottom).

Table 3. Oxidation potentials of the ferrocene derivatives ($E_{1/2}$ in V vs SCE) in DCM; rate constants for the quenching processes (in air-equilibrated toluene); estimated values of ΔG for reductive electron transfer. Data refer to processes involving 3.2 nm and 5.0 nm SiNCs.

		3.2 nm SiNCs		5 nm SiNCs	
Quencher	E _{1/2} / V (vs SCE)	$k_q / 10^8 M^{-1} s^{-1}$	$\Delta G / eV$	$k_q \ / \ 10^6 \ M^{-1} \ s^{-1}$	$\Delta G / eV$
Me ₁₀ -Fc	- 0.02	12.0	- 0.46	27.2	- 0.48
Me ₂ -Fc	+ 0.39	1.30	- 0.05	0.21	- 0.07
Fc	+ 0.51	0.12	+ 0.07	0.02	+ 0.05

From the best fitting for 3.2 nm SiNCs, the reorganization energy $\Delta G^*(0)$ is 8.2 x 10^{-2} eV, the electronic transmission coefficient **k** is ca 10^{-5} , the reduction potential E(*SiNC/SiNC⁻) is + 0.44 V and E(SiNC/SiNC⁻) is - 1.18 V in DCM vs SCE (since E₀₀ = 1.62 eV). It is appropriate to mention that other quenchers with less accessible oxidation potentials than ferrocene have been tested, but in those cases no quenching of SiNCs luminescence has been detected.

The rate constants obtained in the case of 5.0 nm SiNCs (Table 3) are lower compared to the cases of 3.2 nm SiNCs. By fitting the data of logk_q values versus oxidation energy of the ferrocene derivatives, the following values were obtained: $E(*SiNC/SiNC^{-}) = + 0.46 \text{ V}$, thus $E(SiNC/SiNC^{-})$ is - 0.84 V (in DCM vs SCE), $\Delta G^*(0)$ is 2.2 x 10^{-1} eV , and the electronic transmission coefficient **k** results around 10^{-6} .

It is worth noting that the electronic transmission coefficients of oxidative and reductive quenching is similar and it is one order of magnitude lower for 5.0 nm compared to 3.2 nm SiNCs, indicating that the main contribution to the nonadiabaticity of the process is related to the nanocrystals, as previously discussed, and not to the molecular quencher.

Conclusions

A series of quinone electron acceptors and ferrocene electron donors were investigated as molecular quenchers of the photoluminescence of SiNCs by oxidative and reductive electron transfers, respectively. The superposition of the Stern-Volmer plots reporting the ratio of luminescence quantum yields or the ratio of lifetimes in the absence and presence of quenchers demonstrates that the quenching process is dynamic, i.e. the quencher molecules are not associated to the SiNCs at the ground state.

The rate constants of the photoinduced electron transfer process were influenced by the reduction potential of the quenchers, the size of the SiNCs, the solvent polarity, but not by the surface capping layer of the SiNCs (dodecyl or ethylbenzene groups), suggesting that quencher molecules can penetrate within the protecting layer. These data were interpreted within the Marcus theory and enabled us to locate the position of the VB and CB, as reported in Figure 5. From the data reported in Figure 5, the band gap energy is ca. 1.9 eV and 1.4 eV, for 3.2 nm and 5.0 nm SiNCs respectively. These values are in good agreement with the corresponding values obtained by optical characterization ($E_{00} = 1.62$ eV for 3.2 nm and 1.30 for 5.0 nm nanocrystals). The small discrepancy can be due to the presence of surface states.



Figure 5. Estimated position of valence (VB) and conduction band (CB) reported in V (vs SCE) for 3.2 nm and 5.0 nm SiNCs.

The analysis of the rate constants enabled us to estimate also the very small intrinsic barrier, a parameter related to the amount of distortion of both the inner coordinates and the outer solvation shells accompanying electron transfer, as well as the electronic transmission coefficient, which evidences a nonadiabatic electron transfer process in all the investigated cases. Therefore, the electron transfer processes observed for very exoergonic reactions are not diffusion controlled. Furthermore, this parameter decreases upon increasing the dimension of SiNCs because photoexcitation of larger SiNCs has a larger probability of forming an internal rather than a surface exciton and thus leads to a lower electronic coupling with the molecular quencher.

To the best of our knowledge, this is the first time in which Marcus theory has been used to rationalize electron transfer processes involving SiNCs. The evaluation of VB and CB position is particularly important in the case of SiNCs since electrochemical investigations are usually not informative: no signal can be recorded by standard cyclic voltammetry, likely due to the thick layer of passivating ligands, as well as to the slow kinetic of electron transfer processes.

ASSOCIATED CONTENT

Supporting Information. Synthetic procedures, photophysical characterization and details on the fitting procedure. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author

* Department of Chemistry "Giacomo Ciamician", University of Bologna, Via Selmi 2, 40126 Bologna, Italy. E-mail: paola.ceroni@unibo.it

Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Funding Sources

This research is supported by the European Commission ERC Starting Grant (PhotoSi, 278912).

Notes

[#]In the present case the work term w can be neglected since it is approximately 0 for the reactants which are uncharged species and it is negligible (< 0.01 eV) for the products.

ACKNOWLEDGMENT

We thank Dr. Vittorio Morandi for the access to the Electron Microscopy facilities and useful discussions.

REFERENCES

- Kovalenko, M. V. Opportunities and Challenges for Quantum (1)Dot Photovoltaics. Nat. Nanotechnol. 2015, 10, 994-997
- (2) Kovalenko, M. V; Manna, L.; Cabot, A.; Hens, Z.; Talapin, D. V; Kagan, C. R.; Klimov, X. V. I.; Rogach, A. L.; Reiss, P.; Milliron, D. J.; Guyot-sionnnest, P.; Konstantatos, G.; Parak, W. J.; Hyeon, T.; Korgel, B. A.; Murray, C. B.; Heiss, W. Prospects of Nanoscience with Nanocrystals. ACS Nano 2015, 9, 1012-1057.
- Marcus, R. a. On the Theory of Electron-Transfer Reactions. VI. (3) Unified Treatment for Homogeneous and Electrode Reactions. J. Chem. Phys. 1965, 43, 679.
- Electron Transfer in Chemistry; Balzani, V., Ed.; Wiley-VCH: (4) Weinheim, 2001.
- Balzani, V.; Scandola, F. Supramolecular Photochemistry; (5) Horwood: New York, 1991.
- (6) Zhu, H.; Yang, Y.; Hyeon-Deuk, K.; Califano, M.; Song, N.; Wang, Y.; Zhang, W.; Prezhdo, O. V.; Lian, T. Auger-Assisted Electron Transfer from Photoexcited Semiconductor Quantum Dots. Nano Lett. 2014, 14, 1263-1269.
- Olshansky, J. H.; Ding, T. X.; Lee, Y. V.; Leone, S. R.; Alivisatos, A. P. Hole Transfer from Photoexcited Quantum (7)Dots: The Relationship between Driving Force and Rate. J. Am. Chem. Soc. 2015, 137, 15567-15575.
- (8) Bang, J. H.; Kamat, P. V. CdSe Quantum Dot - Fullerene Hybrid Nanocomposite for Solar Energy Conversion : Electron Transfer and Photoelectrochemistry. ACS Nano 2011, 5, 9421.
- Virkki, K.; Demir, S.; Lemmetyinen, H.; Tkachenko, N. V. (9) Photoinduced Electron Transfer in CdSe/ZnS Quantum Dot-Fullerene Hybrids. J. Phys. Chem. C 2015, 119, 17561-17572.
- (10)Huang, J.; Mulfort, K. L.; Du, P.; Chen, L. X. Photodriven Charge Separation Dynamics in CdSe/ZnS Core/shell Quantum Dot/cobaloxime Hybrid for Efficient Hydrogen Production. J. Am. Chem. Soc. 2012, 134, 16472-16475.
- Tvrdy, K.; Frantsuzov, P. A.; Kamat, P. V. Photoinduced (11)Electron Transfer from Semiconductor Quantum Dots to Metal Oxide Nanoparticles. Proc. Natl. Acad. Sci. USA 2011, 108, 29-34
- Dasog, M.; Kehrle, J.; Rieger, B.; Veinot, J. G. C. Silicon (12)Nanocrystals and Silicon-Polymer Hybrids: Synthesis, Surface Engineering, and Applications. Angew. Chemie - Int. Ed. 2016, 55. 2322-2339.
- McVey, B. F. P.; Tilley, R. D. Solution Synthesis, Optical (13) Properties, and Bioimaging Applications of Silicon

Nanocrystals. Acc. Chem. Res. 2014, 47, 3045-3051.

- (14)Mastronardi, M. L.; Henderson, E. J.; Puzzo, D. P.; Ozin, G. A. Small Silicon, Big Opportunities: The Development and Future of Colloidally-Stable Monodisperse Silicon Nanocrystals. Adv. Mater. 2012, 24, 5890-5898.
- (15)Yi, Y.; Zhu, G.; Liu, C.; Huang, Y.; Zhang, Y.; Li, H.; Zhao, J.; Yao, S. A Label-Free Silicon Quantum Dots-Based Photoluminescence Sensor for Ultrasensitive Detection of Pesticides. Anal. Chem. 2013, 85 (23), 11464-11470.
- (16)Gonzalez, C. M.; Iqbal, M.; Dasog, M.; Piercey, D. G.; Lockwood, R.; Klapötke, T. M.; Veinot, J. G. C. Detection of High-Energy Compounds Using Photoluminescent Silicon Nanocrystal Paper Based Sensors. Nanoscale 2014, 6, 2608-2612.
- Content, S.; Trogler, W. W. C.; Sailir, M. J.; Sailor, M. Detection of Nitrobenzene , DNT , and TNT Vapors by (17)Quenching of Porous. Chem. Eur. J. 2000, 6, 2205-2213.
- (18)Mazzaro, R.; Locritani, M.; Molloy, J. K.; Montalti, M.; Yu, Y.; Korgel, B. A.; Bergamini, G.; Morandi, V.; Ceroni, P. Photoinduced Processes between Pyrene-Functionalized Silicon Nanocrystals and Carbon Allotropes. Chem. Mater. 2015, 27, 4390-4397.
- (19) Romano, F.; Yu, Y.; Korgel, B. A.; Bergamini, G.; Ceroni, P. Light-Harvesting Antennae Based on Silicon Nanocrystals. Top. Curr. Chem. 2016, 374, 1-18.
- Ding, Z.; Quinn, B. M.; Haram, S. K.; Pell, L. E.; Korgel, B. a; (20)Bard, A. J. Electrochemistry and Electrogenerated Chemiluminescence from Silicon Nanocrystal Quantum Dots. Science 2002, 296, 1293-1297.
- (21) Bae, Y.; Lee, D. C.; Rhogojina, E. V; Jurbergs, D. C.; Korgel, B. a; Bard, A. J. Electrochemistry and Electrogenerated Chemiluminescence of Films of Silicon Nanoparticles in Aqueous Solution. Nanotechnology 2006, 17, 3791-3797.
- (22)Wolf, O.; Dasog, M.; Yang, Z.; Balberg, I.; Veinot, J. G. C.; Millo, O. Doping and Quantum Confinement Effects in Single Si Nanocrystals Observed by Scanning Tunneling Spectroscopy. Nano Lett. 2013, 13, 2516-2521.
- (23) Montalti, M.; Credi, A.; Prodi, L.; Gandolfi, M. T. Handbook of Photochemistry; CRC Press: Boca Raton, 2006.
- (24)Trumpower, B. L. Function of Quinones in Energy Conserving Systems; Accademic Press, Inc., New York U.S.A., 1982.
- (25)Hohlein, I. M. D.; Kehrle, J.; Helbich, T.; Yang, Z.; Veinot, J. G. C.; Rieger, B. Diazonium Salts as Grafting Agents and Efficient Radical-Hydrosilylation Initiators for Freestanding Photoluminescent Silicon Nanocrystals. Chem. Eur. J. 2014, 20, 4212-4216.
- (26)Bank, Howard M.; Cifuentes, Martin E.; Martin, T. E. Process for the Synthesis of Soluble, Condensed Hydrodosilicon Resins Containing Low Levels of Silanol. 5,010,159, 1991.
- Buriak, J. M. Illuminating Silicon Surface Hydrosilylation: An (27)Unexpected Plurality of Mechanisms. Chem. Mater. 2014, 26, 763-772
- (28)Huck, L. A.; Buriak, J. M. Toward a Mechanistic Understanding of Exciton-Mediated Hydrosilylation on Nanocrystalline Silicon. J. Am. Chem. Soc. 2012, 134, 489-497.
- (29)Wen, X.; Zhang, P.; Smith, T. A.; Anthony, R. J.; Kortshagen, U. R.; Yu, P.; Feng, Y.; Shrestha, S.; Coniber, G.; Huang, S. Tunability Limit of Photoluminescence in Colloidal Silicon Nanocrystals. Sci. Rep. 2015, 5, 12469.
- (30) Hessel, C. M.; Reid, D.; Panthani, M. G.; Rasch, M. R.; Goodfellow, B. W.; Wei, J.; Fujii, H.; Akhavan, V.; Korgel, B. A. Synthesis of Ligand-Stabilized Silicon Nanocrystals with Size-Dependent Photoluminescence Spanning Visible to Near-Infrared Wavelengths. Chem. Mater. 2012, 24, 393-401
- (31)Locritani, M.; Yu, Y.; Bergamini, G.; Baroncini, M.; Molloy, J. K.; Korgel, B. A.; Ceroni, P. Silicon Nanocrystals Functionalized with Pyrene Units: Efficient Light-Harvesting Antennae with Bright Near-Infrared Emission. J. Phys. Chem. Lett. 2014, 5, 3325-3329.
- (32)Fermi, A.; Locritani, M.; Di Carlo, G.; Pizzotti, M.; Caramori, S.; Yu, Y.; Korgel, B. A.; Bergamini, G.; Ceroni, P. Light-Harvesting Antennae Based on Photoactive Silicon Nanocrystals Functionalized with Porphyrin Chromophores. Faraday Discuss. 2015, 185, 481-495.
- (33) V. Balzani, P. Ceroni, A. J. Photochemistry and Photophysics; Wiley-VCH, Weinheim, 2014.
- Sandrini, D.; Gandolfi, M. T.; Maestri, M.; Bolletta, F.; Balzani, (34)V. Electron-Transfer Quenching of the Luminescence of

ACS Paragon Plus Environment

18

19

20

21

22

23

24

25

26

27

28

29

30

31

32

33

34

35

36

37

38

39

40

41

42

43

44

1

2

55 56

57

58

59

60

Ruthenium and Osmium Polypyridine Complexes by cobalt(III) Complexes. *Inorg. Chem.* **1984**, *23*, 3017–3023.

- (35) Marcus, R. a. Exchange Reactions and Electron Transfer Reactions Including Isotopic Exchange. *Discuss. Faraday Soc.* 1960, 29, 21–31.
- Balzani, V.; Moggi, L.; Manfrin, M. F.; Bolletta, F.; Laurence, G. S. Quenching and Sensitization Processes of Coordination Compounds. *Coord. Chem. Rev.* 1975, *15*, 321–433.
- (37) Sandrini, D.; Maestri, M.; Belser, P.; Von Zelewsky, A.; Balzani, V. Kinetic Parameters for the Electron-Transfer Quenching of the Luminescent Excited State of ruthenium(II)-Polypyridine Complexes by Aromatic Amines in Acetonitrile Solution. J. Phys. Chem. 1985, 89, 3675–3679.
- (38) Ballardini, R.; Varani, G.; Indelli, M. T.; Scandola, F.; Balzani, V. Free Energy Correlation of Rate Constants for Electron Transfer Quenching of Excited Transition Metal Complexes. J. Am. Chem. Soc. 1978, 100, 7219–7223.
- (39) Scholes, G. D.; Jones, M.; Kumar, S. Energetics of Photoinduced Electron-Transfer Reactions Decided by Quantum Confinement. J. Phys. Chem. C 2007, 111, 13777–13785.
- (40) Marcus, R. A.; Sutin, N. Electron Transfers in Chemistry and Biology. *Biochim. Biophys. Acta* 1985, 811, 265–322.
- (41) Herkstroeter, W. G. The Triplet Energies of Azulene, Carotene, and Ferrocene. J. Am. Chem. Soc. **1975**, 97, 4161–4167.



