Polydopamine/ethylenediamine nanoparticles embedding a photosynthetic bacterial Reaction Center for efficient photocurrent generation

Gabriella Buscemi\(^1,2\), Danilo Vona\(^1\), Roberta Ragni\(^1\), Roberto Comparelli\(^2\), Massimo Trotta\(^2\)*, Francesco Milano\(^3\) and Gianluca Maria Farinola\(^1\)*.

Dr. Gabriella Buscemi, Dr. Danilo Vona, Dr. Roberta Ragni, Prof. Gianluca Maria Farinola
\(^1\)Chemistry Department, University of Bari “Aldo Moro”, via Orabona 4, I-70126 Bari, Italy
Dr. Roberto Comparelli, Dr. Massimo Trotta
\(^2\) CNR-IPCF, Istituto per i Processi Chimico Fisici / Consiglio Nazionale delle Ricerche via Orabona 4, I-70126 Bari, Italy.
Dr. Francesco Milano
\(^3\) CNR-ISPA, Institute of Sciences of Food Production, S. P. Lecce-Monteroni, I-73100 Lecce

\(\psi\): these two authors contributed equally

E-mail: massimo.trotta@cnr.it; francesco.milano@cnr.it; gianlucamaria.farinola@uniba.it

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Photoactive bio-hybrid soft nanoparticles are obtained by embedding the *Rhodobacter sphaeroides* Reaction Center (RC) in polydopamine (PDA) suspended aggregates and treating them with ethylenediamine (EDA). Such PDA:EDA@RC nanoparticles are investigated for photocurrent generation in photoelectrochemical cells, capable to convert sunlight into electrical energy. The photosynthetic protein retains its structural and functional integrity in the nanostructures and the PDA:EDA@RC nanoparticles exhibit better water dispersity, improved light collection ability and higher photocurrent generation compared to the PDA@RC precursors, where the reaction center is embedded in pure PDA. The hybrid soft nanoparticles incorporating the RC bacterial photoenzyme show charge separated state generation comparable to that of the pristine enzyme in solution, overcoming the main limitation of RC encapsulation in pure PDA, which is the polymer low light transmission ability. As a consequence, photocurrents obtained by RC within the PDA:EDA environment are almost doubled with respect to the PDA@RC. The bio-hybrid composites described here represent an interesting example of effective functional nanostructures for sunlight
photoconversion based on a biological component addressed in a tunable bio-compatible polymer composite, also showing the potentialities of fine chemical tailoring of polydopamine bio-interfaces.

1. Introduction

Bio-hybrid nanostructures based on photoenzymes from photosynthetic organisms, which are able to efficiently convert solar light into charge separated states, open up new concepts in the design of sustainable systems for solar energy conversion.\(^1\)

In particular, bacterial reaction centers (RC), such as the RC obtained from the purple photosynthetic bacterium *Rhodobacter (R.) sphaeroides*, have raised interest for these applications since they are easy to isolate and purify and they can be handled outside their native environment without loss of functionality.\(^2\)

More in detail, the bacterial RC as the one used in this study\(^3\) is a membrane spanning protein composed of three subunits non-covalently bound to a series of cofactors arranged in two symmetrical branches A and B (Figure 1).

**Figure 1.** (a) RC subunit scaffold and cofactor arrangement (PDB 2j8c\(^4\)); (b) steady state absorption spectrum of RCs (upper panel) and light-dark spectrum, recorded under continuous saturating UV light using the protein in the dark state as baseline (lower panel).
Upon photoexcitation, a dimer (D) of bacteriochlorophylls absorbing at 865 nm transfers, with remarkable unitary quantum yield, an electron along the A branch to a bacteriochlorophyll (absorbing at 800 nm), then to a bacteriopheophytin (absorbing at 760 nm) and finally to the so-called quinone acceptor complex composed of two ubiquinone-10 (UQ$_{10}$) molecules located in the Q$_A$ and Q$_B$ pockets, respectively. The ratio of the band absorbance at 760, 800 and 865 nm is 1:2:1 in the intact protein. The final charge separated state (either D$^+Q_B^-$ or D$^+Q_A^-$ if the Q$_B$ site is blocked or empty) has deep absorption minimum at 865 nm in the light-dark difference spectrum suitable to study the protein photoactivity. In the presence of the physiological electron donor cytochrome c$_2$, or artificial donors such as ferrocene and derivatives, RC photoactivation leads to a fully reduced and fully protonated UQ$_{10}H_2$ molecule at the Q$_B$ site, that leaves the pocket and can be replaced by another UQ$_{10}$ or analogous ubiquinone molecules present in solution. Such photocycle is often exploited in photoelectrochemical cells,\cite{1b, 5} capable to convert sunlight into electrical energy. The photocycle can be reproduced using isolated RC suspended in direct,\cite{2a, 6} or inverse micellar systems,\cite{7} but it can also be used embedded and protected in biomimetic environments such as liposomes\cite{8} and giant vesicles,\cite{9} or in nonconventional solvents.\cite{10} Among the systems for embedding functional RC molecules, we have explored polydopamine (PDA) for its many attracting features.\cite{11}

Polydopamine (PDA) is a melanin-like adhesive material deriving from the spontaneous oxidative polymerization of dopamine (DA) in mild basic oxygenated aqueous solutions.\cite{12} PDA is based on 5,6-dihydroxy-indole repeating units and $\pi$-$\pi$ stacking of dopamine monomers, but its chemical structure is very complex and not yet fully elucidated.\cite{12a} One of the reasons of interest for PDA is due to its extraordinary ability to easily form biocompatible, stable, adhesive films with tunable thickness on a large variety of both hydrophobic and hydrophilic substrates.\cite{13} Moreover, further chemical modifications can be carried out using the hydroxyl and amino functional groups on PDA film surface. PDA has been also reported
as a promising precursor of a large variety of materials including nanospheres grown around sacrificial templates,\[^{14}\] used to immobilize enzymes and cells and protect them from surrounding environment. Interestingly, PDA not only forms surface adhered films, but also solution suspended nanoparticles (NPs) whose diameter can be controlled tuning DA polymerization conditions such as pH, temperature and monomer concentration.\[^{15}\] Like in films, also PDA NPs surface can be further modified via metal coordination, electrostatic interactions, covalent or hydrogen bonding, π–π stacking,\[^{16}\] for a variety of applications ranging from biomedicine to sensing.\[^{17}\]

However, PDA NPs are subjected to sedimentation and show optical opalescence and a dark color due to strong light absorption. All these drawbacks can limit their use, especially when light is used to trigger the desired function of systems based on a (bio)active species embedded in or coupled with PDA NPs.

Recently, a treatment with ethylenediamine (EDA) has been shown to induce a controlled degradation of PDA, promoting NPs size reduction and significant changes of their absorption and emission properties.\[^{18}\] In fact, EDA can convert some diketo- forms of the dihydroxy-indole units of PDA in Schiff bases functionalities, and it can react via Michael-like addition with some catechol rings,\[^{19}\] thus disrupting PDA nanostructure by interfering with π-π stacking between the aggregate polymeric chains (Scheme 1).

**Scheme 1.** Schematic drawing of the reaction between EDA and PDA.
Compared to the pristine polymer, the resulting product exhibits improved water dispersibility and photoluminescence due to particles size reduction. Furthermore, PDA:EDA nanoparticles retain the biocompatibility of PDA, and remain suitable to interface biological components.\cite{18}

In our recent work,\cite{11} we reported a straightforward strategy to embed the photosynthetic reaction center (RC) from \textit{R. sphaeroides} in PDA films deposited onto ITO electrode. By simultaneous one-pot PDA polymerization and encapsulation of fully active protein, we reported a photoelectrode based on the bacterial RC immobilized in a much easier and effective way than most of the previously reported methods. Besides the formation of PDA films with embedded RC, (PDA@RC) film, we also observed that PDA generates colloidal nanoaggregates incorporating RC molecules and, in appropriate conditions, the protein is entrapped without loss of functionality.

The issue of high scattering and dark color of PDA@RC nanoparticles prompted us to explore the possibility to perform their controlled degradation with EDA treatment. Considering that the RC photoactivity depends on light harvesting,\cite{20} we expected that the decrease of PDA@RC suspension turbidity by EDA would have effectively enhanced the function of the confined protein.

Starting with the above described background, our study has led to building soft hybrid nanostructures based on PDA:EDA composites incorporating the bacterial RC and to testing their photoconversion ability in photoelectrochemical cells. The investigation has been performed assessing the following points: a) the effective size reduction and turbidity decrease of the PDA@RC nanoparticles upon EDA treatment without losses of encapsulated protein in the PDA:EDA@RC product; b) the biocompatibility of the reaction towards RC structural integrity and functionality; c) the positive impact on the RC light collecting capability and photoactivity (including photocurrent generation) by the improved optical features of the modified polymer.
Our investigation has led to show that PDA:EDA@RC NPs are an interesting biohybrid system for solar energy conversion. Moreover, we envisage that the strategy adopted in this work could be applied also to different protein classes, paving the way to new routes for tailoring PDA nanoparticles as biocompatible carriers for biomacromolecules.

2. Results and discussion

2.1 Preparation and photophysical characterization of PDA, PDA@RC, PDA:EDA, PDA:EDA@RC nanoparticles.

Nanoparticles of PDA and PDA@RC were prepared as detailed in the Experimental Section. As shown in Figure S1, all RC was embedded in PDA nanoparticles. EDA was added at different concentrations (1 – 500 mM) to both PDA and PDA@RC samples to produce a series of PDA:EDA and PDA:EDA@RC nanoparticles with reduced size versus their precursors. In fact, EDA was reported to interfere with the π-π stacking of PDA chains, partially disrupting the polymeric cross-linking, and eventually tuning its photophysical properties such as light absorption and emission.

Figure 2 shows the pictures and UV-vis-NIR absorption spectra of all stages (crude mixture, supernatant and resuspended pellet) of the different reactions between PDA@RC and EDA at increasing concentration. Figure 2a shows that increasing the EDA concentration, a reduction of the dark color of crude mixtures and resuspended pellet is observed, while an opposite trend occurs in the supernatant. The centrifugation at 5000 × g allows to isolate different amounts of pellet depending on EDA concentration; in fact, EDA reduces particle sizes influencing their distributions in the pellet and supernatant. Increasing the EDA concentration and working at the same centrifugation conditions, the amount of pellet is gradually decreased (Figure 2a). The UV-vis-NIR absorption spectra of crude mixtures (Figure 2b) can be regarded as the result of combination of various light absorption contributions from: RC (mainly in the 760-900 nm range), PDA (whose absorption is nearly constant in the
investigated range), the EDA induced modification of PDA nanostructure (more evident below 600 nm and proportional to the EDA concentration) and light scattering (inversely proportional to the EDA concentration) occurring in all suspensions. The presence of an isosbestic-like region in the 450-500 nm range further confirms a conversion of the dark grey PDA polymer to a reddish PDA:EDA reaction product, whose contribution to absorption differs from that of bare EDA in solution (Figure S2). Figure 2c, relevant to supernatants, shows the absence of scattering and negligible presence of RC in all samples with the exception for the 500 mM EDA derived sample. Moreover, light absorption below 600 nm, increasing with EDA concentration, indicates that supernatants are rich of PDA:EDA small nanoparticles, deriving from partial PDA degradation, that do not precipitate under the selected centrifugation conditions. According to the literature,[18] we also found that nanoparticles in supernatants obtained by treatment with EDA are photoluminescent, with emission peaks tunable with EDA concentration (1-500 mM) in the 495-565 nm range (Figure S3).

Figure 2d shows that light scattering in the resuspended pellets is slightly lower than the corresponding crude mixtures, while light absorption below 600 nm is significantly reduced, as expected considering that small PDA:EDA reddish nanoparticles are mainly present in the supernatant. Resuspended pellets include almost entirely the RCs (90-96%) up to the 100 mM EDA treated sample, while at 500 mM EDA, all the protein remains in the supernatant, likely embedded in PDA:EDA nanoparticles that are too small to be precipitated upon centrifugation. Moreover, in this last case, a partial denaturation of RC is observed (Figure 2c, dark blue line) as the bands in the NIR region are no longer in the optimal 1:2:1 ratio.
2.2 Morphological characterization of nanoparticles by DLS and SEM

We selected 100 mM as the optimal EDA concentration leading to PDA:EDA@RC nanoparticles with the lowest scattering contribution and the highest RC content preserving its structural integrity. The morphological characterization was performed by both dynamic light scattering (DLS) and scanning electron microscopy (SEM) measurements.

Figure 3 shows DLS size distributions of bare PDA, PDA:EDA, PDA@RC and PDA:EDA@RC, dispersed in T_{25}. An increase of the particles average size is observed, passing from 930 ± 200 for bare PDA to 1170 ± 240 for PDA@RC particles. After 100 mM EDA treatment, all the hydrodynamic diameters decrease, with average size values set at 670 ± 180 for PDA:EDA and 870 ± 150 for PDA:EDA@RC. These results are in agreement with those expected considering the relevant absorption spectra (Figure S4), since the
characteristic increase of absorbance upon decrease of wavelengths is more evident for PDA@RC than for PDA, whereas a less evident difference is observed in absorption spectra of PDA:EDA@RC and PDA:EDA.

![Absorption Spectra](image)

**Figure 3.** Hydrodynamic diameter distributions obtained by DLS for PDA, PDA:EDA, PDA@RC, PDA:EDA@RC recorded at 25°C.

SEM micrographs of PDA (**Figure 4a**) and PDA:EDA (**Figure 4b**) show an evident decrease (from 500 ± 100 nm to 350 ± 100 nm) of the average size after EDA treatment. **Figure 4c** shows that RC induces micrometric clusters in the PDA@RC sample (see arrow) responsible also for the higher hydrodynamic radius observed in the DLS measurement. The PDA:EDA@RC particles in **Figure 4d** exhibit reduced sizes with respect to PDA@RC and after deposition both nanoparticles and a film-like structure (see arrows) are visible. A statistical image analysis of the nanoparticles, after separation of the larger clusters, confirms a decrease of PDA@RC particles after the EDA treatment from 350 ± 100 to 160 ± 60 nm (p value < 0.05 by Anova validation).
Figure 4. SEM images of (a) PDA, (b) PDA:EDA, (c) PDA@RC (arrow: aggregates) and (d) PDA:EDA@RC (arrows: film-like material). Scale bar: 2 µm.

2.3 Photoactivity investigation of embedded RC by transient absorption

Transient absorption measurements (TA) were carried out to investigate the RC photoactivity in PDA@RC and PDA:EDA@RC samples (both for crude mixtures and resuspended pellets) obtained by treatment with EDA at different concentrations (1 - 500 mM). The amount of embedded RC that can be photoexcited is assessed monitoring the absorbance changes at 865 nm,[21] where the band of the RC dimer is bleached upon formation of the charge separated state, as detailed in the Experimental Section. Light intensity was set to a subsaturating value in order to excite about 40 % of bare RC, with the aim to study the optical filtering effects of PDA and PDA:EDA coatings.
Figure 5. (a) Amount of charge separated state obtained for RC, PDA@RC and PDA:EDA@RC from 100 mM EDA (resuspended pellets); (b) histogram summarizing TA data for all PDA:EDA@RC samples (filled bar for crude mixtures, striped bar for resuspended pellets). All data refer to 1 µM RC under white light (350-600 nm) illumination.

Figure 5a refers to TA measurements for detergent-solubilized RC, and resuspended pellet of PDA@RC and PDA:EDA@RC from 100 mM EDA, while Figure 5b summarizes the experimental data of the complete series of samples, where the activity of detergent-solubilized RC was set as 100%.

In PDA@RC, only 44% and 50% of RC can be photoexcited in crude mixture and in resuspended pellets, respectively. The higher photo-excitability of RC in resuspended pellets versus crude mixtures is also observed in all EDA treated samples. Moreover, as the EDA concentration increases, slight differences are noticed up to 10 mM EDA compared to unmodified PDA, while substantial improvements are obtained starting from 50 mM EDA reaching the maximum value of 83% photo-exciteable RC at 100 mM EDA. These results can
be rationalized considering the progressive decrease of suspension turbidity. Finally, at 500 mM EDA the photoactivity of RC in the crude mixture is reduced to 39 % as a consequence of partial photoenzyme denaturation, while the resuspended pellet shows negligible photoactivity due to the lack of a significant amount of RC (Figure 2d).

2.4 Photocurrent generation by PDA@RC and PDA:EDA@RC nanoparticles.

The ability of PDA@RC and PDA:EDA@RC to produce photocurrents has been explored. The photocycle in bacterial RC photoenzyme involves the reduction of ubiquinone-10 in the Q_b pocket to ubiquinol, that occurs with the simultaneous oxidation of two cytochrome c^{2+} proteins. We used a photoelectrochemical cell (PEC) with a classical three-electrode configuration to measure the photocurrent generated in RC-based systems, using FcMeOH as organometallic electron donor instead of cytochrome and decylubiquinone (dQ) as electron acceptor in place of UQ_{10}, both having suitable redox potential and chemical reactivity. Upon illumination a photocurrent can be recorded as the result of the reaction at the electrodes interface of light generated oxidated and reduced forms of mediators. Depending on the reaction that occurs at WE, the photocurrent can be cathodic or anodic, with conventional negative or positive sign, respectively.[22].

PDA@RC and PDA:EDA@RC (100 mM EDA) resuspended pellets were diluted to 0.3 µM RC final concentration, in 100 mM phosphate buffer with Triton X-100 at pH 7 (P_{100}TX_{0.03}). The obtained photocurrents are shown in Figure 6.

In our case, the negative sign of photocurrent indicates that a cathodic process is occurring at the WE, i. e. the reduction of FcMeOH^{+} photo-oxidized species. As an effect of EDA, the signal intensity is almost doubled from ~ 0.3 µA/cm^{2} for PDA@RC to ~ 0.5 µA/cm^{2} for PDA:EDA@RC. The increase of photocurrent is in agreement with the improved production of charge separated state of RC embedded in PDA:EDA (Figure 5a).
Figure 6. Photocurrents of 0.3 µM RC in PDA@RC and PDA:EDA@RC (100 mM EDA). P₁₀₀TX₀.₃ pH 7, 0.3 mM FcMeOH, 0.1 mM dQ.

3. Conclusion

In conclusion, we have explored the effects of EDA on morphological and photophysical properties of polydopamine nanoparticles embedding the bacterial photosynthetic Reaction Center. Tuning the EDA concentration, a controlled reduction of PDA particles size was obtained, as well as a variation of the optical features of the polymer, having a strong effect on the encapsulated protein photoactivity. More in detail, PDA:EDA@RC nanoparticles obtained by 100 mM EDA are characterized by an higher water dispersity, light collection, photoactivity and photocurrent generation compared to their PDA@RC precursors. PDA:EDA@RC appear intriguing soft bio-nanostructures for photocurrent generation in photoelectrochemical cells, and therefore interesting novel model biohybrids for solar energy conversion, whose properties can be finely tailored by varying the polymer composition. On a more general perspective, our study can be envisioned as an example of how chemical tuning of soft bio-hybrid structures can be an effective route to new systems for solar energy conversion based on photosynthetic microorganisms components.

4. Experimental Section
Chemicals. The reagents for the phosphate buffer solutions, dQ, FcMeOH, Triton X-100 (TX), tris-(hydroxymethyl)-aminomethane (Tris), ethylenediamine and dopamine hydrochloride were purchased from Sigma. All aqueous solutions were prepared using water obtained by Milli-Q Gradient A-10 system (Millipore, 18.2 MΩ cm, organic carbon content ≤4 µg L⁻¹). ITO glass slides of $8 \times 9 \times 0.7$ mm³ with ~ 10 Ω sq⁻¹ surface resistivity and a transmittance > 85% were washed in 5% Hellmanex solution, rinsed with bidistilled water and finally washed in acetone.

Preparation of RC. Reaction Centers were purified from the purple photosynthetic bacterium *R. sphaeroides* strain R26 following the procedure described by Isaacson.\(^23\) Protein purity is established by the absorbance ratio at 280 nm ($A_{280}$) and 802 nm ($A_{802}$), which was kept at $A_{280}/A_{802} < 1.4$ while the absorbance ratio $A_{760}/A_{865}$ was kept ≤ 1. The ubiquinone content on average was about UQ₁₀/RC =1.8.

Preparation of PDA and PDA@RC nanoparticles:
PDA nanoparticles were prepared dissolving dopamine hydrochloride 1.0 mg in 1 mL of Tris-HCl buffer (25 mM, pH 8.8) ($T_{25}$). The mixture was stirred at room temperature for 5 hours under atmospheric oxygen exposure to allow dopamine polymerization. A similar procedure was carried out for PDA@RC preparation except for the presence of RC 1 µM suspended in the $T_{25}$ buffer, and the reaction mixture was kept either in the dark or under green light to avoid protein light stress. PDA and PDA@RC nanoparticles were isolated as pellets by centrifugation at 5000 × g for 10 minutes and resuspended in $T_{25}$ buffer (1 mL).

Both polymerization reactions were monitored recording the UV-vis-NIR absorption spectra for: (i) the reaction mixture immediately after the addition of dopamine; (ii) the final reaction mixture after polymerization; (iii) the supernatant and (iv) the pellet after centrifugation. Complete RC encapsulation into PDA was confirmed by the absence of the typical RC absorption peak at 802 nm in the supernatant.

Preparation of PDA:EDA and PDA:EDA@RC nanoparticles.
The PDA and PDA@RC pellets obtained according to the previously described procedure were suspended in 1 mL T25 and ethylenediamine was added to obtain different concentrations (1, 10, 50, 100, 500 mM). The reaction mixtures were stirred overnight at room temperature under dark in a closed vial. PDA:EDA and PDA:EDA@RC nanoparticles were respectively pelleted by centrifugation at 5000 × g for 10 minutes and resuspended in T25 buffer (1 mL).

RC concentration in PDA:EDA@RC is calculated by the characteristic absorption band at 802 nm (ε = 288 ± 14 mM⁻¹ cm⁻¹) after the subtraction of the suspension scattering. For easier comparison, data are normalized to the protein concentration using the follow equation:

\[
\% \text{RC}_{\text{pellet}} = \frac{A_i - A_f}{A_i} \cdot 100
\]

Where \(A_i\) is the absorbance at 802 nm of the reaction mixture before centrifugation, \(A_f\) is the absorbance at 802 nm of the resuspended pellet.

**Scanning electron microscopy.** For SEM analysis, ITO substrates (1 cm²) were washed twice in acetone and ethanol, sonicated and dried. The suspensions of PDA, PDA:EDA, PDA@RC and PDA:EDA@RC were deposed directly onto ITO substrates, dried overnight and dehydration was completed dipping the substrates in a series of fresh ethanol solutions. A Zeiss Sigma (Oberkochen, Germany) field emission and scanning electron microscope operating in the 0.5–20 KV range and equipped with a secondary electron detector and back diffusion was used for the characterization. Low accelerating voltage set to 5 KeV was exploited. Samples were mounted onto double sided carbon tape and grounded with silver paste. Image J software was used for average sizes calculations, and results were statistically evaluated via ANOVA.

**Electrochemical measurements:** electrochemical measurements were performed with a three-electrode cell with an Autolab potentiostat PGSTAT 10. The reference electrode was a micro Ag/AgCl electrode and the counter-electrode was Pt wire, while the working electrode (WE)
was an ITO covered glass slide whose area immersed in the electrolytic solution was 0.7 cm$^2$.
The support electrolyte was phosphate 100 mM, TX-100 0.03% pH 7.0 (P$_{100}$TX$_{0.03}$), supplemented with FeMeOH 300 µM as electron donor and dQ 100 µM as electron acceptor together with the PDA@RC and PDA:EDA@RC suspension. A bias of -0.15 V (corresponding to the OCV of the cell in the dark) was applied between the reference and the working electrodes. The light source for the photocurrent generation was a 2.6 W LED emitting at 800 nm providing an irradiance of 25 mW cm$^2$. Light/dark cycles of 50 s were applied.

*Equipment.* Optical spectra in the range 350-1200 nm were recorded using a Cary 5000 UV-Vis-NIR spectrophotometer (Agilent Technologies Inc. – USA). Transient absorption measurements were performed using a kinetic spectrophotometer of local design,[24] based on a 50 W QTH lamp, a Jobin Yvon H10 IR monochromator and a Hamamatsu R928 photomultiplier (Hamamatsu Photonics K.K., Hamamatsu City, Japan). A 250 W QTH lamp was used for continuous light excitation, placed at 90° with respect to the probe beam. A digital oscilloscope (Tektronix TKS3200) was used to collect the resulting data.

The percentage of RC embedded in PDA and PDA:EDA particles that can be photoactivated versus the bare RC, upon illumination with the 250 W QTH light source (filtered with a 350-600 bandpass filter), was calculated as it follows:

\[
\% \text{RC}_{emb/bare} = \frac{\Delta A_{RC_{emb}}}{\Delta A_{RC_{bare}}} \cdot 100
\]

Where $\Delta A$ is evaluated at 865 nm and is proportional to the amount of D$^+$QA$^-$ charge separated state generated upon illumination.

Dynamic Light Scattering (DLS) measurements were performed with a Nanosizer ZS (Malvern instruments) for the determination of the size distribution of particles suspended in T$_{25}$. DLS measurements were performed in backscattering mode at pre-fixed detector angle.
Steady state Fluorescence emission spectra were obtained using a Varian Cary Eclipse fluorescence spectrophotometer ($\lambda_{exc}$ 415 nm, excitation/emission slits 5/5).

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Photoactive bio-hybrid soft nanoparticles are obtained by embedding the *Rhodobacter sphaeroides* Reaction Center (RC) in polydopamine (PDA) suspended aggregates and treating them with ethylenediamine (EDA). Such PDA:EDA@RC nanoparticles are investigated for photocurrent generation in photoelectrochemical cells, capable to convert sunlight into electrical energy.

**Polydopamine/ethylenediamine nanoparticles embedding a photosynthetic bacterial Reaction Center for efficient photocurrent generation**

*Gabriella Buscemi*¹,², *Danilo Vona*¹, *Roberta Ragni¹, Roberto Comparelli²*, *Massimo Trotta²*, *Francesco Milano³* and *Gianluca Maria Farinola¹*.

¹: these two authors contributed equally
Supporting Information

Polydopamine/ethylenediamine nanoparticles embedding a photosynthetic bacterial Reaction Center for efficient photocurrent generation

Gabriella Buscemi¹,², Danilo Vona¹, Roberta Ragni¹, Roberto Comparelli², Massimo Trotta²*, Francesco Milano¹* and Gianluca Maria Farinola¹*.

¹Chemistry Department, University of Bari “Aldo Moro”, via Orabona 4, I-70126 Bari, Italy
²CNR-IPCF, Istituto per i Processi Chimico Fisici / Consiglio Nazionale delle Ricerche via Orabona 4, I-70126 Bari, Italy.
³CNR-ISPA, Institute of Sciences of Food Production, S. P. Lecce-Monteroni, I-73100 Lecce

*: these two authors contributed equally

E-mail: massimo.trotta@cnr.it; francesco.milano@cnr.it; gianlucamaria.farinola@uniba.it

Figure S1 UV-Vis-NIR absorption spectra of RC and dopamine, PDA@RC crude mixture and resuspended pellet. All samples are measured in T25 buffer.
Figure S2 UV-Vis-NIR absorption spectra of 500 mM EDA in T$_{25}$ buffer.

Figure S3 Pictures and emission spectra of PDA:EDA@RC supernatant obtained after EDA treatment with increasing amount of EDA (1-500 mM). All samples are measured in T$_{25}$ buffer. $\lambda_{exc} = 415$ nm

Figure S4 UV-Vis-NIR absorption spectra of PDA, PDA:EDA, PDA@RC and PDA:EDA@RC resuspended pellet in T$_{25}$ buffer.