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Calixarene assembly with enhanced photocurrents using P(SNS-NH₂)/CdS nanoparticles structure modified Au electrode systems

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Two novel calix[n]arene-adorned gold electrodes producing high photocurrent intensities were successfully constructed by embedding gold electrode surfaces with both P(4-(2,5-di(thiophen-2-yl)-1H-pyrrol-1-yl)benzenamine) conducting polymer and 4-mercaptopboronic acid-functionalized semiconductor CdS nanoparticles to facilitate the binding of calix[n]arene sulfonic acids with nanoparticles. This structure enabled an electron transfer

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cascade that both induced effective charge separation and efficiently generated photocurrent. The prepared electrodes were used to generate photocurrent by relying on the host-guest interactions of guests Br_3^- and I_3^- , which if positioned well in the system was able to fill electron-hole pairs of CdS nanoparticles. As a result, host calixarene derivatives crucially held Br_3^- and I_3^- ions at a substantial distance from CdS nanoparticles. Furthermore, the effects of various calixarenes on the photocurrent obtained indicate that the system's generation of photocurrent intensities depends on the cavity sizes of calixarene derivatives, which provide an essential center for Br_3^- and I_3^- ions.

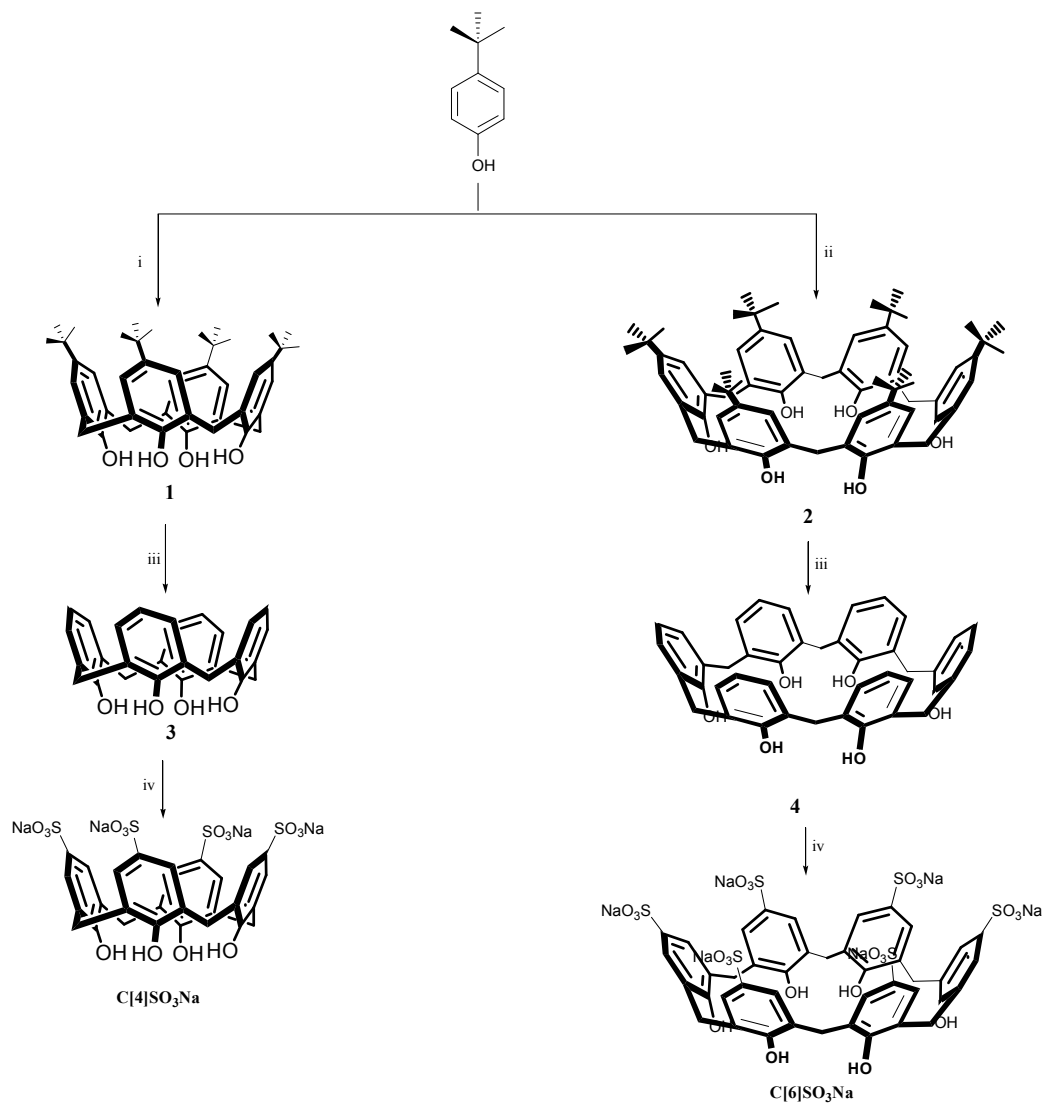
1. Introduction

Preparation of semiconductor nanoparticles (NPs)-modified electrodes has attracted much attention among designers and developers of effective solar cells.^{1,2} Recently, methods have been devised to embed different semiconductor nanoparticles in electrodes; these methods involve the electrophoretic deposition of NPs, the layer-by-layer deposition of NPs by electrostatic attraction or hydrogen binding, the covalent binding of functionalized particles with electrodes, and complementary biomolecular interactions that bridge NPs with electrodes.³⁻⁸ As a result, semiconductor NPs with significant fluorescence quantum yields and robust photostability have proven promising with bioimaging, chemical sensors, photocurrent generation, and biosensors.⁹⁻¹²

During the past decade, great efforts have also been made to develop efficient, stable systems for generating photocurrent via the conversion yield of light energy to electrical energy. Willner et al.¹² prepared a structure enabling an electron-transfer cascade that induced charge separation and generated photocurrent. In their system, along with surface-functionalized gold electrodes with semiconductor CdS NPs, β -cyclodextrin was used as a host to hold donor I_3^- by way of host-guest interactions affording a high local concentration of the hole scavenger and that eliminated rapid electron-hole recombination at the surface of CdS NPs.¹²

Calixarenes are a class of cyclooligomers consisting of a condensation reaction between phenol and formaldehyde.¹³⁻¹⁵ Given their easy preparation, unlimited functionalization, and production of different cavity-sized derivatives, calixarenes have proven to be useful organic compounds, chiefly as selective vehicles for enzyme-mimics,

solid-phase support materials, ion carriers, drug-delivery agents, ion selective electrodes, chemical sensors, biosensors, and catalysis applications.¹⁴⁻¹⁸



Scheme 1 Synthesis of calix[n]arene-*p*-sulfonates. Reaction conditions: i) HCHO, NaOH; ii) HCHO, KOH; iii) AlCl₃, Phenol; iv) H₂SO₄.

To the best of our knowledge, however, no study has yet described the effects of the cavity sizes of water-soluble calixarenes as hosts in systems relying on the creation of an enormous electron-transfer cascade by means of the conversion yield of light energy to electrical energy. In these systems, P(4-(2,5-di(thiophen-2-yl)-1H-pyrrol-1-yl)benzenamine)

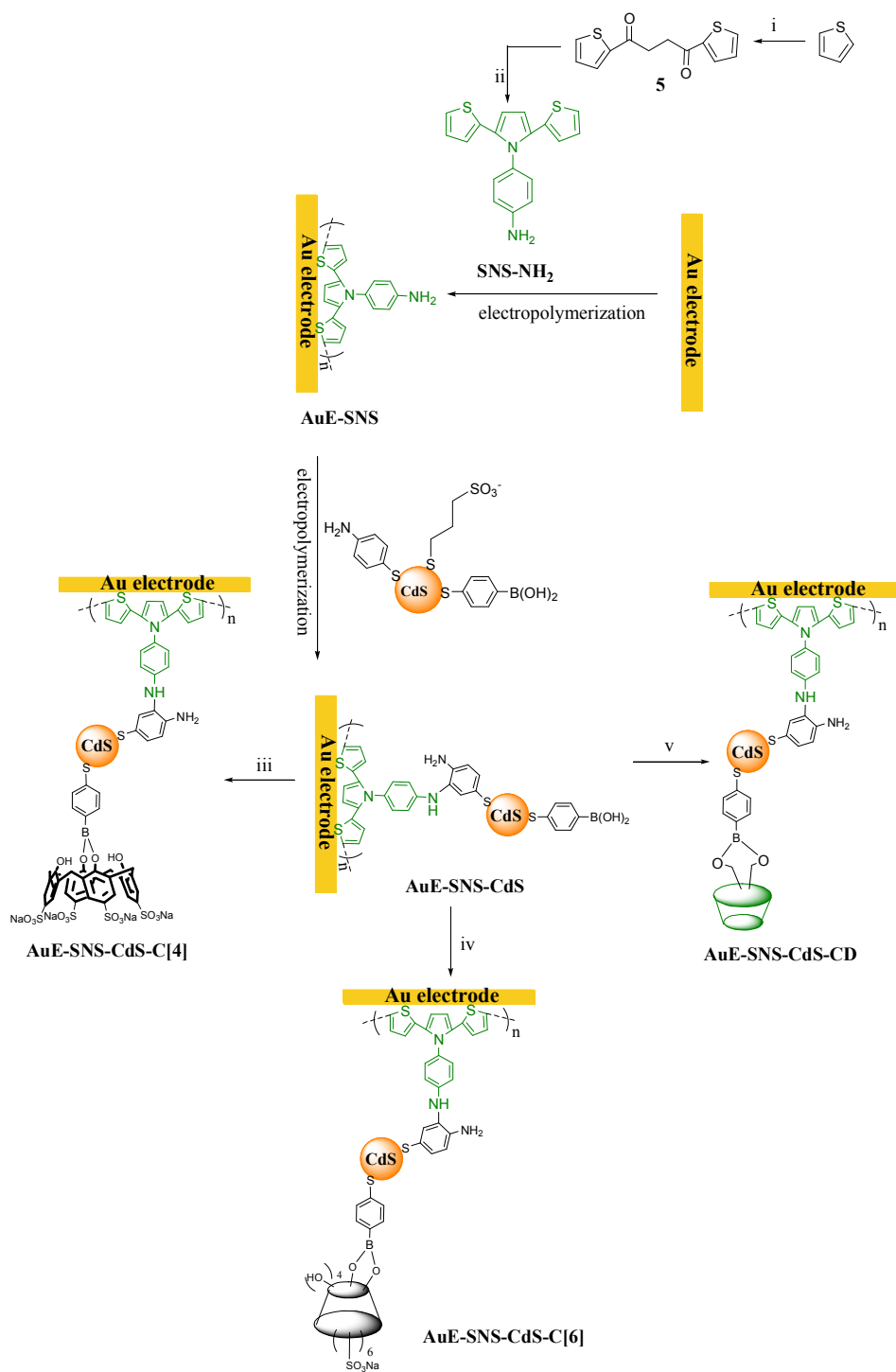
(PSNS-NH₂) conducting polymers embedded onto the gold electrode act as complementary hole transport material, while semiconductor CdS NPs act as the electron acceptor and electron transport material. Along with polymer and semiconductor CdS NPs-embedded gold electrode, two different cavity sizes of calix[n]arene-*p*-sulfonate derivatives were employed as bridges to induce significant electron transport generated by the donor Br₃⁻ and I₃⁻ guests.

2. Results and discussion

Inspired by reports of systems relying on charge separation, this study sought to improve photocurrent generation in semiconductor CdS NPs coupled with Au electrodes by electron relay bridges or charge-transporting molecular wires. β-cyclodextrin bridging units used in that system were also discovered as receptor sites that concentrated electron donor I₃⁻ at the surface of semiconductor CdS NPs. Given similar tendencies of calixarenes with cyclodextrins against ions, the present work introduces supramolecular assembly depending mostly on host-guest interactions in the system with the primary aim to induce charge-separation and improve photocurrent generation. A conducting polymer was also used in this system to accelerate electron transportation to Au electrodes. For this purpose, the synthesis of calix[n]arene derivatives and conducting monomer SNS-NH₂ was accomplished according to the procedure displayed in Schemes 1 and 2.

Succinyl chloride was treated with thiophene in the presence of AlCl₃ in suitable reaction conditions to produce thiophene-1,4-diketone in an 80% yield.¹⁹ A ring closure reaction of diketone with 1,4-diaminobenzene produced 4-[2,5-Di(2-thienyl)-1*H*-1-pyrrolyl]aniline.²⁰

To determine the cavity effects of calix[n]arenes on host-guest complexation against I₃⁻, C[4]SO₃Na and C[6]SO₃Na were synthesized using the strategies presented in Scheme 1;²¹ C[4]SO₃Na and C[6]SO₃Na were synthesized by the reaction of calix[4]arene and/or calix[6]arene with H₂SO₄.²² Following the previous studies, the structures of all synthesized compounds were assigned on the FTIR, ¹H-NMR, ¹³C NMR, and LC-MS.²²



Scheme 2 Preparation of functionalized Au electrodes (**AuE-SNS-CdS-C[4]**, **AuE-SNS-CdS-C[4]**, **AuE-SNS-CdS-C[6]**, and **AuE-SNS-CdS-CD**). Reaction conditions: i) succinyl chloride, AlCl₃; ii) 1,4-diaminobenzene, propionic acid; iii) calix[4]arene-p-sulfonate; iv) calix[6]arene-p-sulfonate; v) β-cyclodextrin.

To prepare **P-SNS-NH₂**-embedded Au electrodes (**AuE-SNS**), Au slides were electrochemically treated with an **SNS-NH₂**-conducting monomer by using a cyclic voltammeter (CV), as done in a previous study.²³ Results showed that the conducting monomer in the presence of CH₃CN/LiClO₄ had two irreversible oxidation peaks at 0.55 and 0.66 V,²³ suggesting that enough monomer radical cation could be produced via electrochemical processes. New redox peaks belonging to the conducting polymer were found along with an increased number of loops.

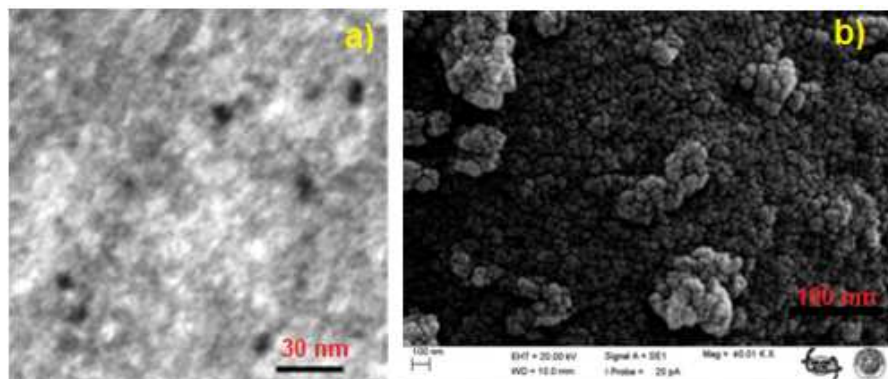
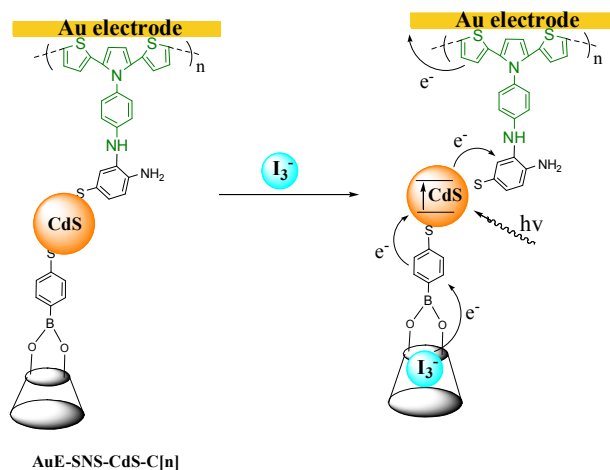


Figure 1 TEM and SEM images of the CdS NPs. (a) TEM image; (b) SEM image.

The preparation of **AuE-SNS** conjugated to calix[n]arenes with semiconductor CdS NPs is presented in Scheme 2. However, the **P-SNS-NH₂**-embedded Au electrode (**AuE-SNS**) was easily modified with 8.5 ± 0.5 nm particle-sized semiconductor CdS NPs (see Figure 1) whose surfaces were functionalized with mercaptoaniline to provide a binding lobe for the embedded electrode and 4-mercaptopboronic acid, both via photoelectrochemical techniques articulated in earlier studies.^{11,24} In order to prepare **AuE-SNS-CdS-C[4]** and **AuE-SNS-CdS-C[6]** systems, calix[n]arene derivatives with two different cavity sized were linked to the free vicinal hydroxyl functions of boronic acid sites on the modified-electrodes according to the adapted procedure.²⁵



Scheme 3 Generation of photocurrent by the AuE-SNS-CdS-C[n] in the presence of I_3^- .

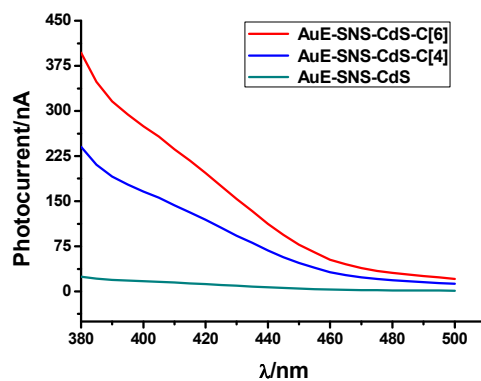


Figure 2 Photocurrent action spectra obtained by AuE-SNS-CdS-C[4], AuE-SNS-CdS-C[6], and AuE-SNS-CdS in the presence of I_3^- (10 mM). All measurements were performed under Ar in an aqueous phosphate buffer solution (0.1 M, Ph 7.4) at 25 °C with a homebuilt photoelectrochemical system including 300 W/m² xenon lamp, monochromator and chopper.

The capacity for photocurrent generation of two **AuE-SNS-CdS-C[4]** and **AuE-SNS-CdS-C[6]** systems were investigated in the presence of electron-donating I_3^- ion. To elucidate the net light intensity absorbed by the semiconductor CdS NPs, two new **AuE-SNS-CdS-C[4]** and **AuE-SNS-CdS-C[6]** systems on the semitransparent Au electrodes were prepared. As shown in Figure 2, **AuE-SNS-CdS-C[6]** had a more significant affinity than both **AuE-SNS-CdS-C[4]** and **AuE-SNS-CdS**. Given the major host-guest interactions of calix[n]arene

derivatives with I_3^- ion, the concentration of the electron donor I_3^- in the calixarene cavities was able to reduce the photogenerated valence-band holes. However, in the absence of the calixarene, the system generated only minor photocurrent, implying that calixarene structure is important for generating high-intensity photocurrent.

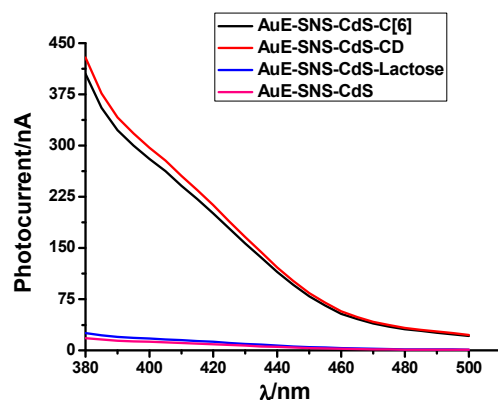


Figure 3 Photocurrent action spectra obtained by AuE-SNS-CdS-C[6], AuE-SNS-CdS-CD, AuE-SNS-CdS-lactose, and AuE-SNS-CdS in the presence of I_3^- (10 mM). All measurements were performed under Ar in an aqueous phosphate buffer solution (0.1 M, Ph 7.4) at 25 °C with a homebuilt photoelectrochemical system including 300 W/m² xenon lamp, monochromator and chopper.

In order to diversify the number of possible donor ions, Br_3^- ion was also employed as an electron-donating group in the photocurrent generation of two **AuE-SNS-CdS-C[4]** and **AuE-SNS-CdS-C[6]** systems. Photocurrent results presented in Figure 4 show that the higher photocurrent generation was obtained when Br_3^- ion used as an electron-donating group, but not more than about 7% if its photocurrent generation value was compared with the obtained results from I_3^- ion. This results indicate that the number of stacked Br_3^- ion in the calixarene holes is more than the number of I_3^- ion. However considering clinical side effect of Br_3^- ion for people, the usage of I_3^- ion would be a good choice for the photocurrent generation systems relying on host-guest interaction.

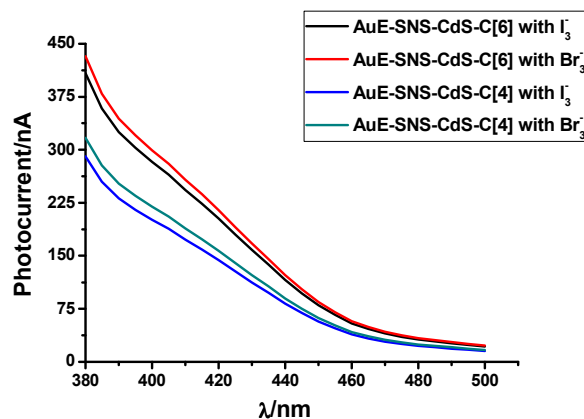


Figure 4 Photocurrent action spectra obtained by AuE-SNS-CdS-C[6], and AuE-SNS-CdS-C[6] in the presence of Br₃⁻ or I₃⁻ (10 mM). All measurements were performed under Ar in an aqueous phosphate buffer solution (0.1 M, Ph 7.4) at 25 °C with a homebuilt photoelectrochemical system including 300 W/m² xenon lamp, monochromator and chopper.

The effect of concentrating I₃⁻ at the semiconductor CdS NPs by means of calix[n]arene-*p*-sulfonates was confirmed by immobilizing **AuE-SNS-CdS** modified with either lactose or β-cyclodextrin to prepare corresponding electrode **AuE-SNS-CdS-lactose** or **AuE-SNS-CdS-CD**, respectively. Figure 3 indicates that the **AuE-SNS-CdS-lactose** system did not bind I₃⁻ ion, meaning that insufficient electron donor concentration was obtained at CdS NPs, though the effect of concentrating I₃⁻ at the semiconductor CdS NPs by way of β-cyclodextrin was readily sufficient. Since the **AuE-SNS-CdS-CD** electrode contains a β-cyclodextrin structure with a cavity size similar to that of calix[6]arene-*p*-sulfonates (see Figure 3),^{26,27} these findings confirm that supramolecular assembly relies on host-guest interaction to generate high-intensity photocurrent by using electron donor I₃⁻ ion.

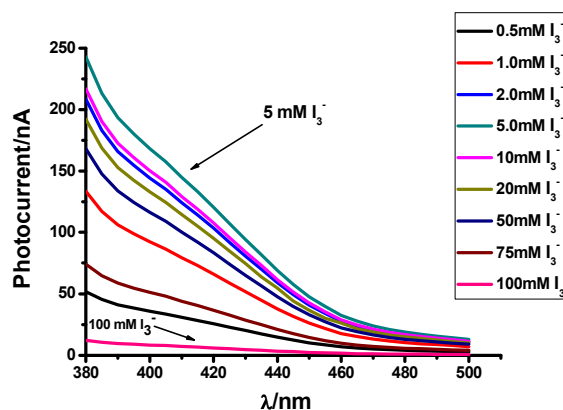


Figure 5 Photocurrent action spectra obtained by AuE-SNS-CdS-C[4] system in the presence of different concentrations of I_3^- ion. All measurements were performed under Ar in an aqueous phosphahte buffer solution (0.1 M, Ph 7.4) at 25 °C with a homebuilt photoelectrochemical system including 300 W/m² xenon lamp, monochromator and chopper.

The optimum concentration for I_3^- ion was also determined by using the AuE-SNS-CdS-C[4] system in the presence of different concentrations depicted in Figure 5. Results clarify that 5 mM concentration of I_3^- ion provides the highest photocurrent.

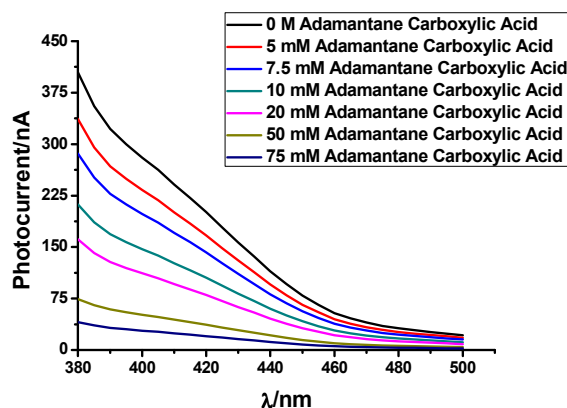


Figure 6 Photocurrent action spectra generated by AuE-SNS-CdS-C[6] system in the presence of various concentrations of adamantane carboxylic acid. All measurements were performed under Ar in an aqueous phosphahte buffer solution (0.1 M, Ph 7.4) at 25 °C with a homebuilt photoelectrochemical system including 300 W/m² xenon lamp, monochromator and chopper.

The role of calix[n]arene-*p*-sulfonates in the concentration of I_3^- ion at the surface of semiconductor CdS NPs in order to generate improved photocurrent was furthered by inhibiting the host-guest complexation consisting of calix[n]arene-*p*-sulfonates and I_3^- ion. It is well known that β -cyclodextrin and calix[n]arene-*p*-sulfonates provide more selectivity toward adamantane carboxylic acid than I_3^- ion.²⁸ In this sense, various concentrations of adamantane carboxylic acid were used in the system (see Figure 6). The obtained photocurrent action spectra indicate that photocurrent intensity decreased when the concentration of adamantane carboxylic acid increased, as consistent with the fact that adamantane carboxylic acid competes with I_3^- ion to form host-guest complexation with calix[6]arene-*p*-sulfonate receptors (see Figure 7).

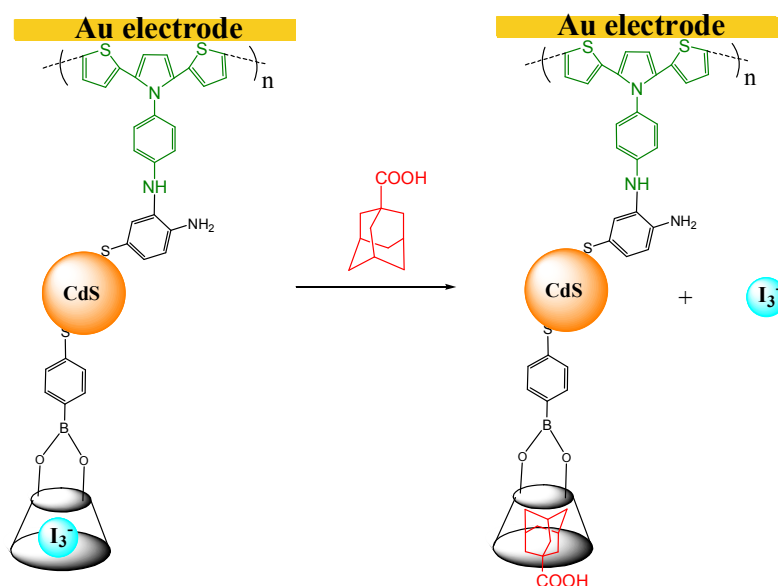


Figure 7 A schematic illustration of selective host-guest interaction.

3. Conclusions

In sum, two novel calix[n]arene receptors with differently sized cavities were successfully conjugated with the free vicinal hydroxyl functions of boronic acid sites of semiconductor CdS NPs modified onto P(4-(2,5-di(thiophen-2-yl)-1H-pyrrol-1-yl)benzenamine) conducting

polymer-embedded electrodes in order to generate high-intensity photocurrent in the presence of electron donor I_3^- ion. Generated photocurrent results indicate that the systems containing calix[n]arene-*p*-sulfonates or β -cyclodextrin enabled both an electron transfer cascade prompting effective charge separation and efficient photocurrent generation. Such photocurrent action reveals that supramolecular assembly relies on strong host-guest interactions of the supramolecular structure with electron donor ions such as Br_3^- and I_3^- ions. Although, the electron-donating Br_3^- ion exhibits higher photocurrent generation than the electron-donating I_3^- ion in our system, the usage of Br_3^- ion causes serious health disorders. Regarding this issue, the experiment depends on an electron-donating I_3^- ion would be a good challenge for the photocurrent generation systems. Moreover, these insights into the generation of intense photocurrent by calix[n]arene-containing systems will open new routes for useful practical applications in the preparation of solar cells.

4. Experimental

4.1. Synthesis

p-*tert*-Butylcalix[4]arene (**1**), *p*-*tert*-butylcalix[6]arene (**2**), calix[4]arene (**3**), calix[6]arene (**4**), calix[n]arene-*p*-sulfonates (**C[4]SO₃Na**, **C[6]SO₃Na**), and 4-(2,5-bis(thiophen-2-yl)-1H-pyrol-1-yl)benzenamine (**SNS-NH₂**) were synthesized as reported previously.^{19-22,29}

4.1.1. Calix[4]arene-*p*-tetrasulfonate (**C[4]SO₃Na**)

White solid. Yield: 70%, mp >350 °C. FTIR (ATR) cm^{-1} : 3133 (ν_{OH}), 1682 (ν_{H_2O}), 1597, 1459 and 1377 ($\nu_{C=C}$), 1151, 1105 (ν_{SO_2} asymmetric), 1023 (ν_{SO_2} symmetric) and 784 (ν_{S-O}). 1H NMR (400 MHz, D_2O): δ 4.15 (s, 8H, ArCH₂Ar), 7.65 (s, 8H, ArH). ^{13}C NMR (100 MHz, D_2O): δ 31.96, 125.97, 126.10, 130.71, 133.36, 156.21. LC-MS calculated for $C_{28}H_{19}Na_5O_{16}S_4$: 854.63, found: 854.94 (see Figure 7).

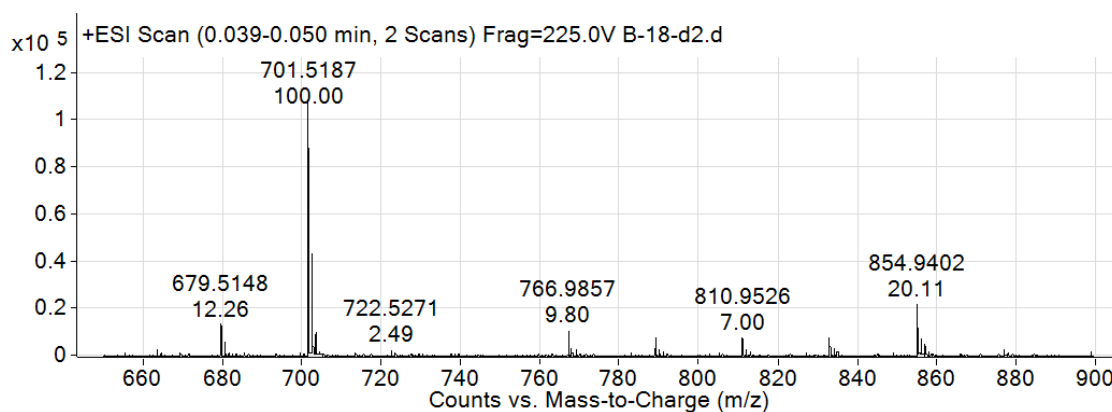


Figure 7 LC-MS spectrum of Calix[4]arene-*p*-tetrasulfonate (C[4]SO₃Na)

4.1.2. Calix[6]arene-*p*-hexasulfonate (C[6]SO₃Na)

White solid. Yield: 40%; mp >350 °C. FTIR (ATR) cm⁻¹: 3154 (ν_{OH}), 1685 ($\nu_{\text{H}_2\text{O}}$), 1591, 1472 and 1340 ($\nu_{\text{C}=\text{C}}$), 1273 ($\nu_{\text{C}-\text{O}-\text{C}}$), 1151, 1108 (ν_{SO_2} asymmetric), 1020 (ν_{SO_2} symmetric), and 870 ($\nu_{\text{S}-\text{O}}$). ¹H NMR (400 MHz, D₂O): δ 3.68 (s, 12H, ArCH₂Ar), 7.23 (s, 12H, ArH). ¹³C NMR (100 MHz, D₂O): δ 32.63, 125.71, 125.80, 129.05, 132.01, 157.95. LC-MS calculated for C₄₂H₂₉Na₇O₂₄S₆: 1270.96, found: 1270.97 (see Figure 8).

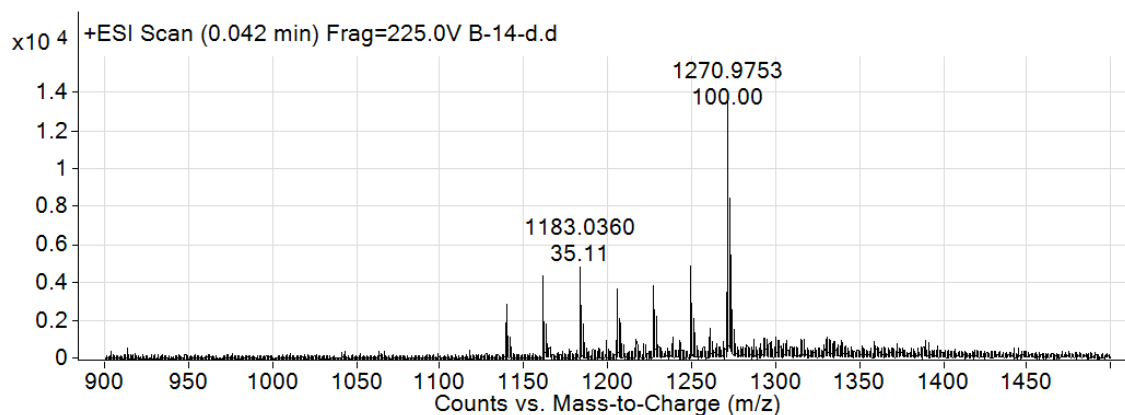


Figure 8 LC-MS spectrum of Calix[6]arene-*p*-hexasulfonate (C[6]SO₃Na)

4.1.3. 4-[2,5-Di(2-thienyl)-1*H*-1-pyrrolyl]aniline (SNS-NH₂)

Grey powder was synthesized in 41% yield, m.p. 187-189 °C. FTIR (ATR) cm^{-1} : 3400 ($\nu_{\text{N-H}}$), 3100 and 3020 ($\nu_{\text{C-H(aryl)}}$), 1550-1380 ($\nu_{\text{C=C(aryl)}}$ and $\nu_{\text{C-N}}$). ^1H NMR (400 MHz, CDCl_3): δ 3.75 (s, 2H, $-\text{NH}_2$), 6.46 (s, 2H, ArH), 6.58 (d, 2H, $J=3.65$ Hz, ArH), 6.73 (dd, 2H, $J=3.65$, 5.10 Hz, ArH), 6.80 (dd, 2H, $J=1.15$, 5.10 Hz, ArH), 6.97 (dd, 2H, $J=6.58$, 2.15 Hz, ArH), 7.12 (dd, 2H, $J=6.58$, 2.15 Hz, ArH). ^{13}C NMR (100 MHz, CDCl_3): δ 109.5, 115.1, 124.2, 124.4, 124.5, 127.0, 129.1, 130.3, 135.7, 146.5.

4.1.4. Preparation of CdS NPs

CdS nanoparticles and functionalized-CdS nanoparticles were prepared according to the literature procedures.^{11b,24} Particle size of the functionalized CdS NPs was determined as 8.5 ± 0.5 nm by using transmission electron microscopy (TEM).

4.2. Modification of the Au electrodes

SNS- NH_2 monomer were interacted with clean Au slides, and polymerized via electrochemically onto it by using a cyclic voltammeter with -0.5 to 1.2 V potential range in the presence of a mixture of NaClO_4 and LiClO_4 in acetonitril according to the literature.^{23,29} 3-Mercaptosulfonate, *p*-mercaptoanilin and 4-mercaptopboronic acid adorned semiconductor CdS NPs were electrochemically coupled with PSNS- NH_2 -modified Au electrode using 60 repetitive cyclic-voltammetry scans with -0.5 to 0.5V potential ranges in 0.1 M phosphate buffer, pH 7.4 according to the literature.¹¹ Both PSNS- NH_2 conducting polymer and semiconductor CdS NPs-embedded Au electrodes were then reacted with a phosphate buffer solution (pH 7.4) that contained calix[n]arene derivatives or β -cyclodextrin or lactose (10 mM for each compound) for a time interval of 2h, to led the binding of the calixarenes to the boronic acid moieties of the functionalized-Au electrodes.

4.3. Photoelectrochemical experiments

Photoelectrochemical experiments¹¹ were carried out using a photoelectrochemical system composed of a 300W Xe lamp (Oriental, model 6258), a monochromator (Oriental, model 74000, 2 nm resolution), and a chopper (Oriental, model 76994). The electrical output from the cell was

sampled by a lock-in amplifier (Stanford Research model SR 830 DSP). The shutter chopping frequency was controlled using a Stanford Research pulse/delay generator model DE535. The currents were measured between the modified Au working electrode and a Pt wire (diameter, $d=0.5\text{mm}$) counterelectrode. For the constant-potential experiments, a three-electrode cell configuration (including an SCE reference electrode) and an external potentiostat/galvanostat (EG&G Model 263) were used. Quartz-crystal microbalance measurements were performed using a home-built instrument linked to a frequency analyzer (Fluke) using Au-quartz crystals (AT-cut 10 MHz). The geometrical area of the Au electrode was $0.2\pm 0.05\text{ cm}^2$.

Acknowledgements

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