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Photocurrent generation of a novel chromoionophore combining D–π–A dye and aza-15-crown-5 ether in LB monolayer films

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A novel amphiphilic chromoionophore, *N*-[4-(2,3,6,7,8,9,11,12-octahydro-5*H*-1,4,10,13,7-benzotetraoxaazacyclopentadecin-7-yl)butyl]-4-{2-[4-(*N*-methyl-*N*-hexadecylamino)phenyl]ethenyl}quinolinium bromide (Crown D), containing a D–π–A styryl dye and an aza-15-crown-5 ether group was synthesized, and successfully transferred onto an indium–tin oxide (ITO) electrode by the Langmuir–Blodgett technique. The effect of different metal cationic subphases on the π–A isotherm of Crown D was investigated. The photoelectric conversion properties of the chromoionophore LB monolayer films were studied. The results show that the photocurrent generation properties of the film strongly depend on the radius of the metal ions coordinated with the aza-15-crown-5 ring of the dye.

Introduction

Since cation binding is sensitive to the ligand environment, the binding equilibrium constant can be effectively controlled by employing a switch-functionalized system where a crown ether is bound intramolecularly to an antenna moiety which is responsive to an external stimulus.[1] Such a switch-functionalized system is a chromoionophore. The chromoionophore is a more sophisticated version of simple crown ether rings. It is composed of two different functional groups: an ionophore, recognizing specific ions, and a chromophore, transducing the chemical information produced by the ionophore–ion interaction into an optical signal.[2] Interest in chromoionophores has increased significantly because they show ion-selective color changes upon complexation and may be useful for sensing devices for metal cations and neutral molecules.[3–11]

The Langmuir–Blodgett (LB) technique allows amphiphilic derivatives of chromoionophores to be built up into organized ultrathin layers.[12] In earlier work, we have found that some donor–π–acceptor (D–π–A) conjugated systems with strong electron donors and acceptors showed good photoelectric conversion (PEC) properties in LB films.[13–21] Here, we chose a D–π–A dye as the antenna and prepared a novel chromoionophore, *N*-[4-(2,3,6,7,8,9,11,12-octahydro-5*H*-1,4,10,13,7-benzotetraoxaazacyclopentadecin-7-yl)butyl]-4-{2-[4-(*N*-methyl-*N*-hexadecylamino)phenyl]ethenyl}quinolinium bromide (Crown D). This molecule was successfully transferred onto an indium–tin oxide (ITO) substrate using the Langmuir–Blodgett technique. We focused on the photoelectric conversion properties of the chromoionophore in LB monolayer films.

Experimental

1. Materials

The synthetic procedure for Crown D is illustrated in Scheme 1. 4-(*N*-Methyl-*N*-hexadecylamino)benzaldehyde was prepared according to the previously reported method.[22] 2,3,6,7,8,9,11,12-Octahydro-5*H*-1,4,10,13,7-benzotetraoxaazacyclopentadecine (Crown A) was synthesized as described in the literature.[23]

7-(4-Bromobutyl)-2,3,6,7,8,9,11,12-octahydro-5*H*-1,4,10,13,7-benzotetraoxaazacyclopentadecine (Crown B). Crown B was synthesized by reaction of Crown A (4.1 mmol) with 1,4-dibromobutane (5 mmol) in absolute ethanol (15 mL) using K_2CO_3 as a base. The product was recystallized from CH_2Cl_2–petroleum ether (1 : 5, v/v). Yield: 62.4%; mp: 95–97 °C. Calc. for $C_{18}H_{28}BrNO_4$ (%): C, 53.74; H, 7.01; N, 3.48. Found (%): C, 53.66; H, 6.93; N, 3.41. ^1H NMR ($CDCl_3$) δ: 7.0–6.8 (4H, m, ArH), 4.2–4.0 (12H, m, -OCH_2-), 4.0–3.8 (8H, m, -CH_2N and -CH_2Br), 2.0–1.6 (4H, m, -CH_2-).

***N*-[4-(2,3,6,7,8,9,11,12-Octahydro-5*H*-1,4,10,13,7-benzotetraoxaazacyclopentadecin-7-yl)butyl]-4-methylquinolinium bromide (Crown C).** Crown C was synthesized as follows: 201 mg (0.5 mmol) Crown B and 715 mg 4-methylquinoline (5 mmol) were dissolved in 10 mL absolute ethanol. After the mixture was refluxed for 24 h, the solvent was evaporated to dryness and the yellow residue was washed with diethyl ether, filtered and dried under vacuum.

Methylviologen diiodide (MV^{2+}) was synthesized by reaction of 4,4′-dipyridyl with methyl iodide. Its identity was confirmed by ^1H NMR analysis. The electrolytes for the electrochemical experiment were LiCl, NaCl, KCl, RbCl and CsCl (Beijing Chemical Factory, China). Hydroquinone (H_2Q) (Beijing Chemical Factory, China) was recrystallized from water before use. The spreading solvent used for monolayer deposition was chloroform (Beijing Chemical Factory, China).

***N*-[4-(2,3,6,7,8,9,11,12-Octahydro-5*H*-1,4,10,13,7-benzotetraoxaazacyclopentadecin-7-yl)butyl]-4-{2-[4-(*N*-methyl-*N*-hexadecylamino)phenyl]ethenyl}quinolinium bromide (Crown D).** Crown D was prepared by condensing Crown C and 179.5 mg (0.5 mmol) 4-(*N*-methyl-*N*-hexadecylamino)benzaldehyde in

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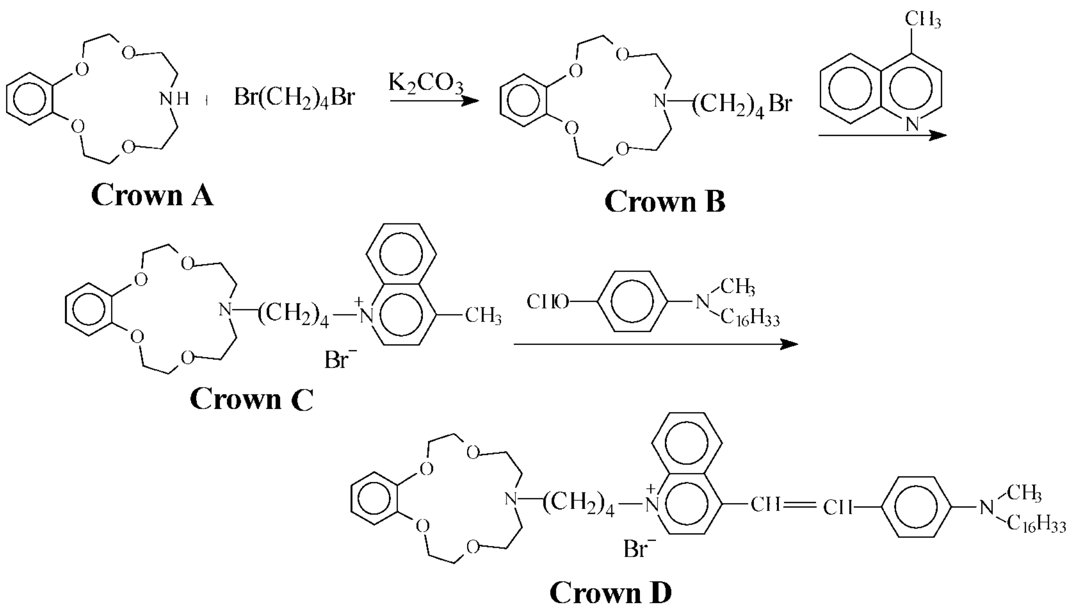


Scheme 1 The synthetic route to Crown D.

absolute ethanol (15 mL) using 0.2 mL piperidine as the catalyst. The mixture was refluxed for 12 h. After cooling to room temperature, the resulting precipitate was filtered and chromatographed (SiO_2, MeOH–$CHCl_3$ = 1 : 12, v/v). Yield: 41.8%; mp: 218–220 °C. Calc. for $C_{52}H_{76}BrN_3O_4$ (%): C, 70.41; H, 8.64; N, 4.74. Found (%): C, 70.82; H, 8.23; N, 4.92. ^{1}H NMR ($CDCl_3$) δ: 0.87 (t, 3H, 1CH_3), 1.09 (m, 26H, 13CH_2), 1.62 (m, 4H, $2NCH_2\mathit{CH}_2$), 1.87 (m, 2H, $1N^+CH_2\mathit{CH}_2$), 2.96–3.18 (m, 11H, $4NCH_2$ and $1NCH_3$), 3.72–4.08 (m, 12H, $6OCH_2$), 4.40 (m, 2H, $1N^+$-CH_2), 6.78–6.92 (m, 8H, Ar-H), 7.08 (d, 1H, 1CH=), 7.67 (d, 1H, 1CH=), 7.82–7.95 (m, 5H, quinolyl), 8.56 (d, 1H, quinolyl).

2. Measurements

C, H, N data of the compounds were obtained by using a Carlo Erba 1106 elemental analyzer. ^{1}H NMR spectra were measured by using a Bruker ARX300 spectrophotometer. Electronic spectra in solution or on LB monolayers were recorded on a Shimadzu model 3100 UV–Vis–NIR spectrophotometer. Melting points were measured on an X4 micromelting point apparatus.

A model 622 NIMA Langmuir–Blodgett trough was employed for the Langmuir–Blodgett study. Water obtained from an EASY pure RF system was used as the subphase ($R \approx 18$ MΩ cm). The ITO slides were all hydrophilically pretreated as previously described.[24] Chloroform solutions of 0.20 mg mL^{-1} Crown D dye were spread drop-by-drop from a chloroform-cleaned, glass microsyringe to the subphase surface (20 ± 1 °C). After 15 min allowing the solvent to evaporate, the floating films were compressed at a ratio of 40 cm^2 min^{-1} and the surface pressure (π)–area (A) isotherms were recorded. For deposition of the monolayer, the hydrophilic pretreated substrates were immersed in the subphase, and then the monolayer was formed at the surface pressure of 30 mN m^{-1} and transfered to ITO substrates with a pulling rate of 5 mm min^{-1}. Films with transfer ratios of 1.0 ± 0.1 were used in the experiments.

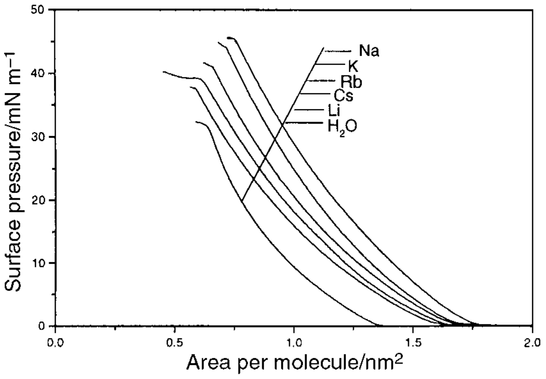


Fig. 1 Surface pressure (π)–molecular area (A) isotherm of Crown D in pure water and metal cationic subphases (20 ± 1 °C).

Photoelectrochemical measurements were carried out in 0.1 M MCl solution (M = Li^+, Na^+, K^+, Rb^+ or Cs^+) using an ITO electrode modified by Crown D LB monolayer films, platinum wire and Ag/AgCl electrode as working electrode, counter electrode and reference electrode, respectively. The effective illuminated area of a flat window for Crown D was 0.8 cm^2. The light source used for the photoelectrochemical study was a 500 W Xe arc lamp. The light beam was passed through a group of filters (*ca.* 400–800 nm, Toshiba Co., Japan, and Schott Co. USA) in order to get a desired bandpass of light. The light intensity at each wavelength was measured with an energy and power meter (Scientech, USA).

Results and discussion

1. LB monolayer properties

A Langmuir film of Crown D was formed on the surface of LiCl, NaCl, KCl, RbCl or CsCl aqueous subphase. Fig. 1 shows the π–A isotherms of Crown D on the different subphases. The limiting area per molecule on the metal cationic subphases ranges from 1.24 to 1.48 nm^2 from extrapolation of the tangent of the π–A isotherms of Crown D at 30 mN m^{-1} (Table 1, A). These values are larger than that

Table 1 The properties of Crown D LB monolayer films

Subphase	Radius of M^+/nm	A^a/nm^2	P/mN m^{-1}	K/N m^{-3} × 10^{17}	$\lambda_{max(f)}$/nm
H_2O	—	1.04	31.6	8.10	560
Li^+	0.68	1.24	37.6	6.24	560
Na^+	0.95	1.48	45.3	6.29	562
K^+	1.33	1.39	43.5	6.49	560
Rb^+	1.48	1.35	41.9	6.04	561
Cs^+	1.69	1.32	41.2	5.61	560

^{a}A: limiting area per molecule; P: collapse pressure; K: slope of the solid phase; $\lambda_{max(f)}$: absorption maximum on LB film.

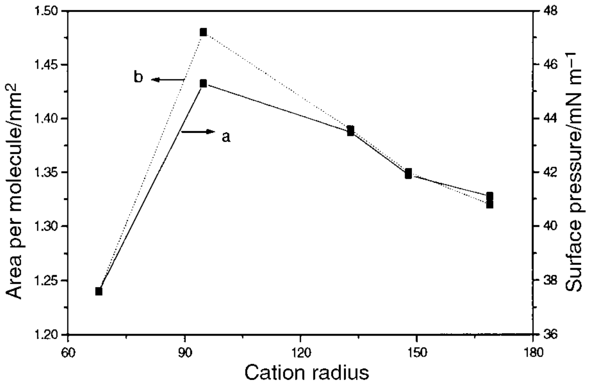


Fig. 2 Effect of the metal cations on the collapse pressure of crown D film and on the molecular limiting area.

obtained from the pure water subphase (1.04 nm^2), which indicates that the interaction of metal cations with the aza-15-crown-5 ether group of Crown D occurs. The collapse pressures of the Crown D LB films on these metal cationic subphases are all over 35 mN m^{-1}, and are larger than that obtained from the pure water. It can be seen from Fig. 2 that the effect of these metal cations on the collapse pressure of crown D film is similar to that on the molecular limiting area.

To better understand the effect of cations on Langmuir film of Crown D, the configurations of Crown D with or without Na cation (as an example) were optimized by the B3LYP/STO3G method, and the charge distributions for the ground state of Crown D and Crown D+Na$^+$ were calculated by using AM1.

Limited by the capacity of the computer, the model molecule having an *N*,*N*′-dimethylamino group on the phenyl ring to form Crown D′ was used for calculation. It appears that the results are valid for reference and comparison. The optimized configurations for Crown D′ and Crown D′+Na$^+$ using by the B3LYP/STO3G method are shown in Fig. 3. When the cavity of the crown is empty, the quinolinium group of Crown D′ is close to the aza-15-crown-5 ring due to their interaction, and the σ-bridge (-CH$_2$.CH$_2$CH$_2$CH$_2$-) linking the quinolinium group and the aza-15-crown-5 ring assumes a compact conformation. However, upon the coordination of Na$^+$ with the aza-15-crown-5, Na$^+$ enters the crown ether ring, and the distance between the quinolinium group and the aza-15-crown-5 ether ring is enlarged because repulsion between the positively charged quinolinium group and the crown-coordinated metal ion causes the σ-bridge to assume an extended staggered conformation. The charge distributions of Crown D′ and Crown D′+Na$^+$ support this point of view. It can be clearly seen from Table 2 that the changes of the net charge distributions in their donor and acceptor parts are apparent, which indicates that the charge rearrangement happens upon coordination. During the charge rearrangement, the net charge of the acceptor part becomes smaller (from 0.418 to 0.367). However, the net charge of the tail part changes from negative (−0.047) to positive (+0.907), leading to the repulsion of the quinolinium group and aza-15-crown-5, thus triggering the conformational change mentioned above.

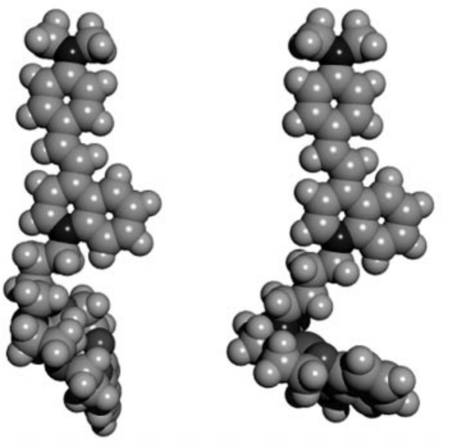


Fig. 3 The optimized configurations of Crown D′ and Crown D′+Na$^+$.

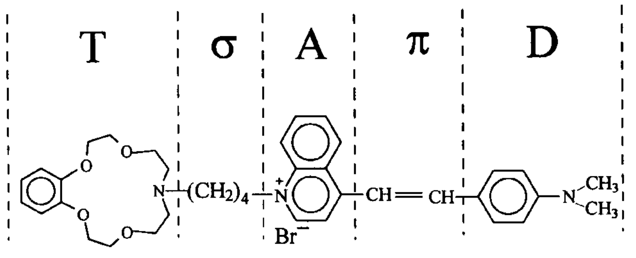
A possible interaction model before and after coordination of Crown D is proposed as shown in Scheme 2. When metal cations with different radii coordinate with aza-15-crown-5, the match extent of their coordination appears different, and subsequently the mutual repulsion between the quinolinium group and the metal cation is different, which makes the effects of the metal cation on the π–A isotherm of Crown D different.

The absorption maximum of crown D in chloroform is at 576 nm. Comparison of the electronic spectra of Crown D LB monolayers with that of Crown D in chloroform solution (Table 1, $\lambda_{\max(f)}$) shows a blue-shift of about 15 nm for LB monolayers of Crown D on pure water relative to different metal cationic subphases, indicating that Crown D forms H-aggregates in these monolayers.[25]

2. Photoelectric conversion properties (PEC)

In the three-electrode photoelectrochemical cell, the ITO electrode modified by Crown D dye can generate photocurrent.

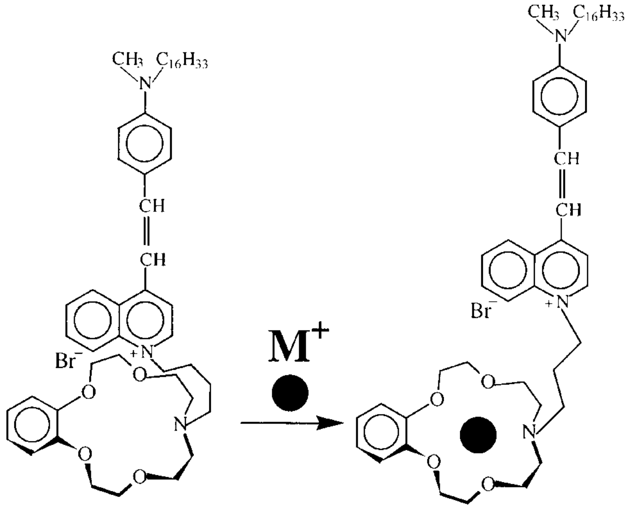
Table 2 The data of charge distribution at the different parts of molecules in the ground state for Crown D′ and Crown D′+Na$^+$



Crown D'

Compd	T[a]	σ[b]	A[c]	π[d]	D[e]	Σ[f]
Crown D′	−0.047	0.354	0.418	0.078	0.198	0.220
Crown D′+Na$^+$	0.907	0.349	0.367	0.093	0.284	0.083

[a] Sum of the net charges of atoms at the tail part. [b] Sum of the net charge of atoms at the σ-bridge part. [c] Sum of the net charges of atoms at the acceptor part. [d] Sum of the net charges of atoms at the CH=CH bridge. [e] Sum of the net charges of atoms at the donor part. [f] Symmetry deviation parameter Σ = A − D.



Scheme 2 The possible interaction of Crown D with the metal cationic subphases.

However, the photoelectric conversion properties of Crown D are different under the different experiment conditions.

2.1. Effect of metal cation electrolyte on PEC.

A photocurrent generation from a Crown D–ITO electrode prepared from the pure water subphase was observed when it was immersed in 0.1 M NaCl (as an example) electrolyte solution under illumination with white light. The direction of the photocurrent changes from anodic to cathodic quickly, then the photocurrent climbs gradually and finally levels off at a maximum value. Here, we refer to the maximum photocurrent as peak current. When the Crown D–ITO electrode was switched off and on again, no further increase in photocurrent was observed as the same maximum value was approached (Fig. 4). When this Crown D–ITO was immersed in pure water for 90 min, the same phenomenon of increasing cathodic photocurrent can be observed with good reproducibility. When the Crown D–ITO, prepared from the pure water subphase, was immersed in 0.1 M NaCl solution for 30 min and was illuminated under white light in 0.1 M NaCl electrolyte solution, a stable cathodic photocurrent with no increase was observed. It can be seen from Table 3 that the value of the peak current of the Crown D–ITO electrode measured in the different 0.1 M MCl solutions (M = Li^+, Na^+, K^+, Rb^+ or Cs^+) is different. The largest peak current was obtained in 0.1 M NaCl electrolyte solution.

The above experiments show that the alkali metal cations in electrolyte solutions coordinate with the aza-15-crown-5 ether group. When the crown D–ITO electrode is immersed in the electrolyte solutions, the metal cation enters the aza-15-crown-5 ether ring, and the positive charge of the azacrown ether ring is enhanced, rendering it a better electron acceptor. Thus, the photocurrent increases. Metal cations with different radii interfere with the antenna differently, and the difference is reflected in the PEC properties of Crown D in different electrolyte solutions. Among the alkali metal cations, Na^+ cation is matched best with aza-15-crown-5, and therefore the peak current of Crown D obtained in the NaCl electrolyte solution is the largest. This means that Crown D is an ion-selective material.

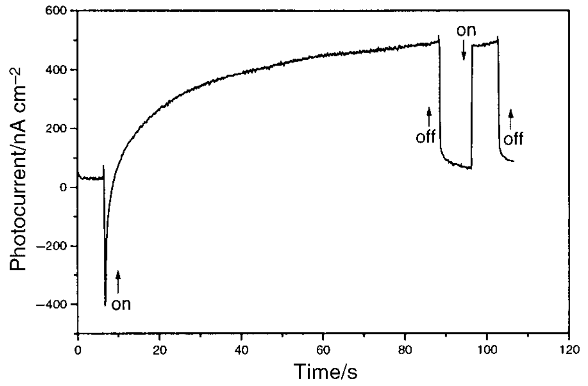


Fig. 4 The photoelectric response of a Crown D–ITO film deposited from pure water subphase in 0.1 M NaCl electrolyte solution under ambient conditions, upon irradiation with 137 mW cm^{-2} white light.

Table 3 The photoelectric conversion properties of a Crown D–ITO electrode in different electrolyte solutions[a]

MCl	I^b/nA cm^{-2}	I^c/nA cm^{-2}	η^c(%)	I^d/nA cm^{-2}	η^d(%)
LiCl	206	9.4	0.25	38.5	1.02
NaCl	435	20.5	0.52	88.2	2.24
KCl	330	15.7	0.40	58.4	1.49
RbCl	243	12.3	0.32	44.3	1.15
CsCl	228	11.8	0.30	41.3	1.05

[a] *I*: peak current per square centimetre; η: external quantum yield. [b] Under irradiation with 137 mW cm^{-2} white light for Crown D, in 0.1 M MCl electrolyte solution containing dissolved O_2. [c] Under monochromatic irradiation at 567 nm from a 137 mW cm^{-2} white light for Crown D, in 0.1 M MCl electrolyte solution containing dissolved O_2. [d] Under monochromatic irradiation at 567 nm from a 137 mW cm^{-2} white light for Crown D, under −100 mV and in 0.1 M MCl electrolyte solution containing dissolved O_2 and 5 mM MV^{2+}.

It can be seen from Fig. 5 that the action spectrum of the cathodic photocurrent for Crown D is similar to the absorption spectrum of the Crown D LB monolayer films, suggesting that the Crown D LB films are responsible for photocurrent generation.[26] The preliminary quantum yield (η) for the photocurrent generation was calculated according to eqns (1) and (2)

$$\eta = i/[eI(1-10^{-A})] \qquad (1)$$

$$I = W\lambda/hc \qquad (2)$$

where *i* is the observed photocurrent, *e* is the charge on an electron, *I* is the number of photons per unit area and unit time, *A* is the absorbance of the LB monolayer, λ is the wavelength of light irradiation, *W* is light power at λ nm, *c* is the velocity of light, and *h* is Planck's constant. In 0.1 M NaCl electrolyte solution with zero bias voltage, about 20.5 nA cm^{-2} photocurrent can be obtained for Crown D under a 567 nm light irradiation which corresponds to an intensity of 5.40×10^{15} photons cm^{-2} s^{-1}. The photoelectric conversion quantum yield for Crown D LB monolayers-modified ITO electrode (the

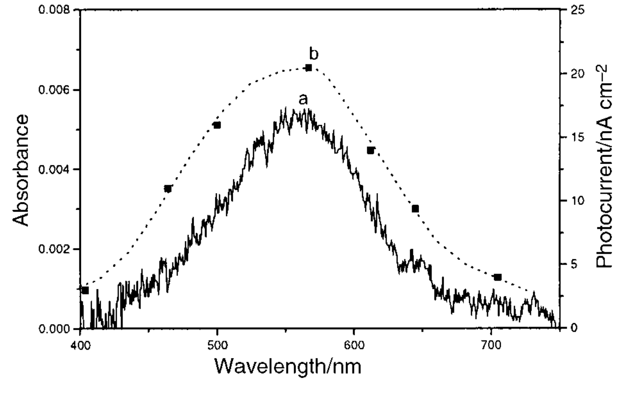


Fig. 5 UV–Vis absorption spectrum (a) of Crown D in LB monolayer films obtained from pure water subphase and the action spectrum (b) of the cathodic photocurrents for Crown D. The intensities of different wavelengths are all normalized.

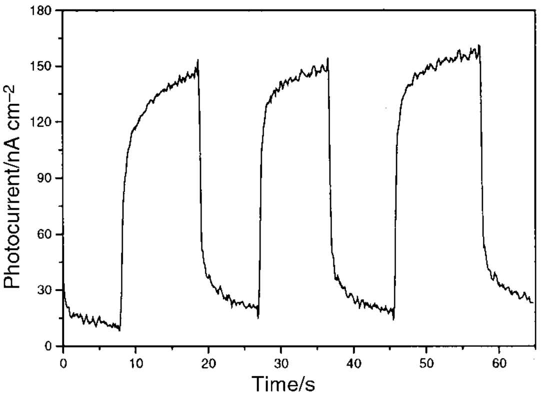


Fig. 6 Photocurrent generation of Crown D–ITO electrode deposited from pure water subphase in 0.1 M Bu_4NBr electrolyte solution under ambient conditions, upon irradiation with 137 mW cm^{-2} white light.

absorbance of the monolayers is about 0.0046 at 567 nm) in NaCl solution is about 0.52%, while the quantum yields in 0.1 M LiCl, KCl, RbCl or CsCl electrolyte solutions are 0.25, 0.40, 0.32 and 0.30%, respectively (Table 3, I, η, columns 3 and 4).

2.2. Effect of metal cationic subphases on PEC. The results show that the photocurrent of Crown D is dependent not only on the electrolyte solution containing different metal cations but also on the subphase containing different metal cations. To investigate the effect of the metal cation subphase on the PEC, we chose the bulky group Bu_4NBr instead of an alkali metal chloride as the electrolyte for photoelectrochemical measurements on Crown D, because alkali metal cations can coordinate with Crown D. Fig. 6 gives the photoelectric response of Crown D in 0.1 M Bu_4NBr solution. It can be seen from Fig. 6 that a relatively stable photocurrent with no climbing photocurrent was obtained for Crown D prepared from pure water subphase. This confirms that Bu_4N^+ does not easily coordinate with the aza-15-crown-5 ether group in Crown D.

Table 4 shows the PEC properties of Crown D prepared from pure water and different metal cation subphases. Because the number of active moieties per unit area in the LB monolayer films is an important factor contributing to the PEC performance, here we use the photocurrent per molecule as the data for comparison. Taking the limiting molecular area into account, the numbers of molecules per square centimetre are 9.71×10^{13}, 8.07×10^{13}, 6.76×10^{13}, 7.19×10^{13}, 7.41×10^{13} and 7.58×10^{14} for Crown D prepared from pure water, LiCl, NaCl, KCL, RbCl and CsCl subphases [Table 4, N(m)], respectively. Consequently, with reference to the photocurrent per square centimetre (see Table 4, I, column 2), one can see that photocurrents per molecule for Crown D prepared from pure water, LiCl, NaCl, KCl, RbCl and CsCl subphases are 1.30×10^{-12}, 1.98×10^{-12}, 3.33×10^{-12}, 2.38×10^{-12}, 2.08×10^{-12}, and 1.95×10^{-12} nA molecule^{-1}, respectively (Table 4, I, column 4), among which the photocurrent of Crown D prepared from NaCl subphase is the largest. Therefore, the metal cation subphase affects obviously the photocurrent generation of Crown D.

Table 4 The photoelectric responsive properties of Crown D–ITO electrode deposited from pure water and metal cationic subphases[a]

Subphase	I^b/nA cm^{-2}	$N(m) \times 10^{13}$	$I_m{}^b \times 10^{-12}$/nA molecule^{-1}
H_2O	126	9.71	1.30
LiCl	160	8.07	1.98
NaCl	225	6.76	3.33
KCl	171	7.19	2.38
RbCl	154	7.41	2.08
CsCl	148	7.58	1.95

[a] I: photocurrent per square centimetre; I_m: photocurrent per molecule; η: external quantum yield; N(m): number of molecules per square centimetre. [b] Under irradiation with 137 mW cm^{-2} white light for Crown D, in 0.1 M NBu_4Br electrolyte solution containing dissolved O_2.

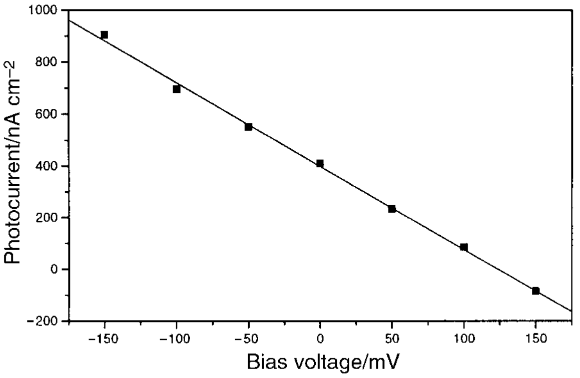


Fig. 7 Photocurrent *versus* bias voltage for a Crown D–ITO electrode in 0.1 M NaCl aqueous solution under ambient conditions, upon irradiation with 137 mW cm^{-2} white light.

2.3. Dependence of PEC on experimental conditions. Since the experimental conditions affect photocurrent generation, an investigation of the relation between the photocurrent generation and the experimental conditions facilitates the understanding of the mechanism of photoelectric conversion. Here, in 0.1 M NaCl electrolyte solution, Crown D–ITO obtained from pure water as an example was investigated. (1) It can be seen from Fig. 7 that a linear relationship exists between photocurrent and bias voltage in the range of +150 mV to −150 mV, indicating that the photocurrent flows in the same direction as the applied negative voltage. (2) The photocurrent response (i_{ph}) on incident light intensity (I) for the Crown D–ITO electrode can be described by the Donovan equation[27] $i_{ph} = KI^m$ ($K = 3.23$, $m = 1$, see Fig. 8), which indicates that the separated charge relaxation process that occurs in the Crown D LB monolayers is unimolecular recombination. (3) The effects of electron donor and acceptor on the cathodic photocurrent for Crown D in 0.1 M NaCl solution show that the addition of electron acceptor (MV^{2+}) increases the cathodic photocurrent and electron donor (H_2Q or N_2) decreases the cathodic photocurrent (even reverses it into the anodic photocurrent) (in Table 5).

Under favorable conditions (−100 mV, dissolved O_2 and 5 mM MV^{2+}), a cathodic photocurrent of 88.2 nA cm^{-2} for Crown D–ITO was obtained upon irradiation at 567 nm; the quantum yield of photoelectric conversion is 2.24% in 0.1 M

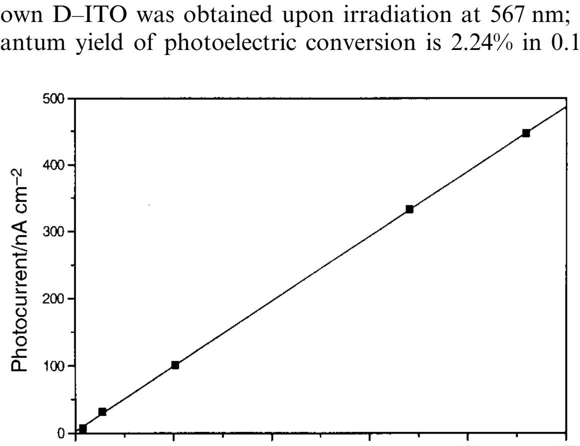


Fig. 8 Dependence of the photocurrent on light intensity for a Crown D–ITO electrode in 0.1 M NaCl electrolyte solution under ambient condition without bias voltage.

Table 5 Effect of donors and acceptors on the photocurrent generation of Crown D–ITO electrode

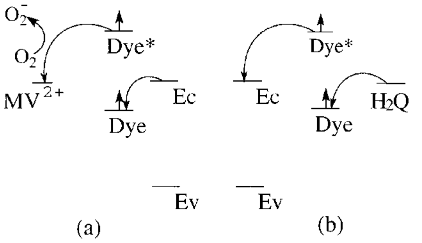
Donor/acceptor	Concn./mM	Photocurrent/nA cm^{-2} [a] Ambient	Photocurrent/nA cm^{-2} [a] N_2 degassed
MV^{2+}	0	424	126
	5	2290	1070
H_2Q	0	436	134
	3.6	-1860^b	-2145^b

[a] Irradiation under 137 mW cm^{-2} white light for Crown D in 0.1 M NaCl solution. [b] "—" indicates anodic photocurrent.

NaCl solution. At the same conditions, the quantum yields for Crown D in 0.1 M LiCl, KCl, RbCl and CsCl solutions are 1.02, 1.49, 1.15 and 1.05%, respectively (see Table 3, I, η, columns 5 and 6).

3. Mechanism of photoelectric conversion

According to the Frank–Condon principle, the only possibility for generating photocurrent under these circumstances is photoinduced electron transfer between the ITO substrate and the excited-state dye within the LB monolayers. With reference to the effects of bias voltage and addition of the electron donor and acceptor in electrolyte solution on the photoelectric conversion behaviors, a possible electron transfer mechanism for Crown D is proposed as shown in Scheme 3. In the presence of some electron acceptors, such as O_2 and MV^{2+} in electrolyte solution, electron transfer from the excited state of Crown D to the electron acceptor occurs, and subsequently an electron from the ITO conduction band is injected into the hole residing in the dye molecules. Thus, cathodic photocurrent is generated. In contrast, if there are strong electron donors in the system, such as H_2Q, a reduced photocurrent and even reversal in the direction of the photocurrent are observed.



Scheme 3 The possible mechanism of photoelectric conversion for Crown D system (a) cathodic photocurrent; (b) anodic photocurrent. * Represents the excited state of the Crown D dye.

Conclusions

We synthesized a novel quinolinium styryl dye containing crown ether (Crown D), and investigated the effect of different metal cationic subphases on the π–A isotherm of Crown D. The photoelectric conversion properties of the crown D LB monolayer film modified ITO electrode are dependent on the nature of the metal ions, no matter whether the metal ions come from the subphase or from the electrolyte solution; these are coordinated with the crown ether attached to the styryl dye. The enhanced photocurrent is attributed to the complex formation of the aza-15-crown-5 group with metal cations. It can thus be concluded that Crown D is an ion-selective photoelectric conversion material.

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