Synthesis and metal ion-sensing properties of fluorescent PET chemosensors based on the 2-phenylimidazo[5,4-*a*]anthraquinone chromophore

Katsuhira Yoshida,*[a] Takayoshi Mori,[a] Shigeru Watanabe,[a] Hideki Kawai[b] and Toshihiko Nagamura[b]

[a] *Department of Chemistry, Faculty of Science, Kochi University, Akebono-cho, Kochi 780-8520, Japan*

[b] *Research Institute of Electronics, Shizuoka University, 3-5-1 Johoku, Hamamatsu 432-8011, Japan*

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Novel fluorescent chemosensors in which an aza-crown is linked to a 2-phenylimidazoanthraquinone fluorophore by a methylene spacer have been synthesized for the sensing of metal cations. A dramatic fluorescence enhancement at 515 nm was observed upon binding of the metal ions, which was interpreted in terms of the control of a photoinduced electron transfer (PET) process. This system can recognize the charge and the size of alkali and alkaline-earth metal cations and can transform its information sensitively and precisely into the magnitude of the enhanced fluorescence.

Introduction

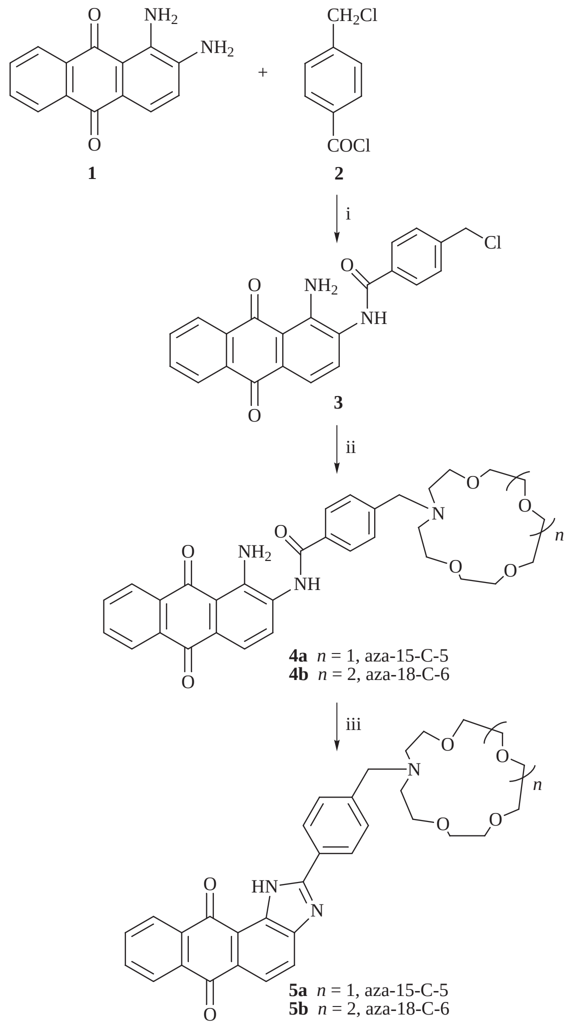
The design and synthesis of fluorescent sensing systems for metal cations and a variety of biologically important species are areas of growing interest because of their potential applications to biomedical and environmental chemosensors[1] or molecular logic devices.[2] Various fluorescent sensors and switches have been reviewed and classified into several types in recent literature.[3]

Chemosensors which apply the principle of photoinduced electron transfer are called PET chemosensors. Fluorescent aromatic hydrocarbons such as anthracene, pyrene, and their derivatives were previously employed for the construction of PET chemosensors with fluorophore–spacer–receptor systems.[1–3] Moreover, fluorescent chromophores such as coumarin,[4] benzimidazobenz[*de*]isoquinolinone,[4] or pyridoimidazopyrazine (PIP)[5] *etc.*, were also found to be valuable resources for the construction of PET chemosensors emitting visible signals. In these cases, the sensing abilities strongly relied on the photophysical and electrochemical properties of the fluorophore. Therefore, research for new fluorophores is indispensable for further development of PET chemosensors.

During the course of our research to develop new fluorophores,[6] we have found that 2-phenylimidazoanthraquinone (PIAQ) emits strong fluorescence at around 515 nm in the visible region. As the chromophoric PIAQ is an effective electron acceptor, it was expected that the PIAQ moiety could be used to construct new PET chemosensors. Hence, we have designed and investigated the metal ion-sensing ability of new fluorescent PET chemosensors in which an aza-crown (AC) is linked to an electron accepting 2-phenylimidazoanthraquinone (PIAQ) fluorophore using a methylene spacer.

Results and discussion

The synthesis of novel fluorescent chemosensors (PIAQ–AC) is outlined in Scheme 1. The reaction of 1,2-diaminoanthraquinone **1** with 4-(chloromethyl)benzoyl chloride **2** in the presence of triethylamine gave the acylation product **3**. The displacement of the chloro atom of **3** by aza-15-crown-5 and



Scheme 1 *Reagents*: i, Et_3N–1,4-dioxane, 60 °C, 7 h; ii, aza-crown, Et_3N–1,4-dioxane, reflux, 25 h; iii, NaOH, 95% EtOH, reflux, 1.5 h.

aza-18-crown-6 ethers in 1,4-dioxane–triethylamine gave the corresponding aza-crowned products **4a** and **4b**, respectively. In order to get the final designed PIAQ–AC chemosensors, **5a** and **5b,** we investigated the intramolecular condensation of **4a** and **4b** under various conditions and found that it proceeds successfully under basic conditions using sodium hydroxide in refluxing ethanol. The structures of **5a** and **5b** were confirmed on the basis of IR, ^{1}H NMR, and elemental analysis. The ^{1}H NMR spectra exhibited a broad singlet signal at around $\delta = 11.25$ ppm, which supports the formation of intramolecular hydrogen bonding between the NH of the imidazole ring and the neighboring quinone carbonyl group. The absorption spectra of PIAQ–AC chemosensors which have a maximum at 405 nm due to a π–π* transition are similar to those of the parent PIAQ chromophore.

The thermodynamic driving force (ΔG_{PET}) calculated by application of the Rehm–Weller equation [eqn. (1)][7] is conveniently

$$\Delta G_{\mathrm{PET}} = E_{\mathrm{ox}} - E_{\mathrm{red}} - e^2/\varepsilon r - E_{00} \qquad (1)$$

used to design PET chemosensors with fluorophore–spacer–receptor systems.[4]

The possibility of intramolecular photoinduced electron transfer from the aza-crown ring to the excited imidazoanthraquinone moiety can be estimated from the ΔG_{PET} value. Hence, we measured the redox potentials of the compound **5a**; cyclic voltammetry was performed in a 1×10^{-3} mol dm^{-3} solution of **5a** in acetonitrile–0.1 mol dm^{-3} $\mathrm{NEt_4^+ClO_4^-}$ at a glassy carbon electrode. The cyclic voltammograms for the reduction of the imidazoanthraquinone moiety showed two reversible one-electron steps and the first and second reduction potentials *vs.* Ag/AgCl were −0.94 and −1.16 V, respectively. With the aza-crown ether moiety, one irreversible oxidation wave was observed at +0.84 V (*vs.* Ag/AgCl). The PIAQ–AC chemosensor **5a** exhibits an absorption band at $\lambda_{\mathrm{max}} = 405$ nm ($\varepsilon_{\mathrm{max}}$ 14,500) and a weak fluorescence emission band at 515 nm. The singlet energy (E_{00}) of the PIAQ chromophore can be calculated as 2.70 eV from the average of the energies of the spectral maxima in absorption and emission. The attractive potential between the radical ion pair $-e^2/\varepsilon r$ is approximately −0.1 eV.[8] Application of these values into eqn. (1) gives the free energy (ΔG_{PET}) as *ca.* −98.4 kJ mol^{-1}, which shows that the photoinduced electron transfer (PET) reaction is highly possible.

The sensing abilities of PIAQ–AC chemosensors, **5a** and **5b**, for alkali and alkaline-earth metal cations have been investigated. Fig. 1 and 2 show the absorption and fluorescence spectral changes upon addition of various metal salts to an acetonitrile solution of **5a**. The patterns of the absorption and emission spectral changes upon binding of the metal ions are fully consistent with those of other PET chemosensors reported in previous papers;[9] that is, the absorption and emission wavelengths and the absorption intensity are substantially unaffected but the emission intensity is significantly changed. Especially, in the case of PIAQ–AC chemosensors, a highly sensitive and dramatic enhancement of fluorescence intensity at 515 nm upon recognition of metal cations was observed. Fig. 3 and 4 show plots of the fluorescence intensity *vs.* the molar ratio of [Metal ion]/[Ligand (**5a** and **5b**)], which indicate 1 : 1 complex formation and strong metal ion binding ability of the chemosensors. The magnitude of the fluorescence enhancement was greatly dependent on both the charge and the size of metal ions with respect to the cavity size[10] of the crown ring. The orders of the fluorescence intensity were $\mathrm{Ca^{2+} > Ba^{2+} > Mg^{2+} \gg Na^+ > Li^+ > K^+}$ for **5a** and $\mathrm{Ba^{2+} > Ca^{2+} > Mg^{2+} \gg K^+ > Na^+ > Li^+}$ for **5b**, respectively. Alkaline-earth metal cations induce much larger enhancement of fluorescence intensity than alkali metal cations. The cation whose size is closer to that of the cavity of the aza-crown seems to exhibit a larger fluorescence enhancement among cations of the same charge. These results confirm that our sensors can recognise the size and the charge of the metal ions and can transform their information precisely into the magnitude of the enhanced fluorescence. Fluorescence quenching was observed upon complexation with metal thiocyanates in the case of PIP–crown chemosensors,[5] which is explained by the PET process from the thiocyanate counter anion to the PIP chromophore. In the case of PIAQ–AC chemosensors, fluorescence quenching by thiocyanate counter anions was not observed. As shown in Fig. 2–4, the fluorescence sensing of the PIAQ–AC chemosensors for metal cations was not disturbed by thiocyanate counter

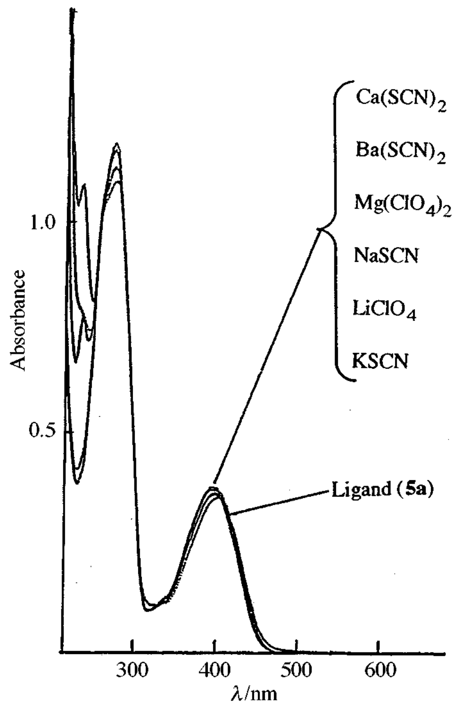


Fig. 1 Absorption spectra of **5a**: before and after addition of metal salts in acetonitrile ([**5a**] = 2.5×10^{-5} mol dm^{-3}, [metal salt] = 1.25×10^{-4} mol dm^{-3}).

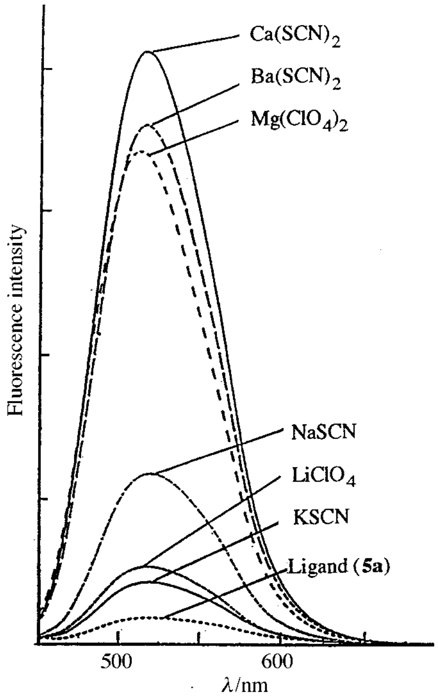


Fig. 2 Fluorescence spectra of **5a**: before and after addition of metal salts in acetonitrile ([**5a**] = 2.5×10^{-5} mol dm^{-3}, [metal salt] = 1.25×10^{-4} mol dm^{-3}, $\lambda_{\mathrm{em}} = 515$ nm, $\lambda_{\mathrm{ex}} = 400$ nm).

anions. The oxidation potential of thiocyanate anion measured by means of cyclic voltammetry shifted from +0.89 to +0.69 V (*vs.* Ag/AgCl) upon complexation of PIAQ–AC with $Ca(SCN)_2$ in acetonitrile solution. From the values, an intermolecular PET from thiocyanate anion to the excited PIAQ chromophore was considered to be possible, because the free energy (ΔG_{PET}) for the PET reaction was estimated to be highly negative, *ca.* -113 kJ mol^{-1}. However, in the case of PIAQ–AC chemosensors, fluorescence enhancement was observed upon addition of metal thiocyanates. The above results suggest that fluorescence quenching by the intermolecular PET process from thiocyanate anion to the excited PIAQ is thermodynamically possible but would be kinetically suppressed.

Using changes in the fluorescence intensity with an increase in the metal ion concentration, the association constants (log *K*) were determined according to the procedure reported by Bourson *et al.*[11] Table 1 summarizes the log *K* values and fluorescence quantum yields (Φ_F) for **5a** and **5b** and their metal complexes. The log *K* values are reasonable in comparison with those known for original aza-crown ethers, aza-15-crown-5 (A15C5), aza-18-crown-6 (A18C6), and diaza-18-crown-6 ($A_2$18C6), with various alkali and alkaline-earth metal cations in the literature[12] as follows: 4.4–4.8 (A15C5–Li^+ in MeCN), 4.7–5.7 (A15C5–Na^+ in MeCN), 3.5–4.5 [A18C6–Na^+ in MeOH (anhydrous)], 4.9–6.0 [A18C6–K^+ in MeOH (anhydrous)], 5.9–6.1 ($A_2$18C6–Ba^{2+} in MeOH), 7 < ($A_2$18C6–Ba^{2+} in MeCN). The log *K* values for the alkali metal ions are smaller than those for the alkaline-earth metal ions, suggesting that the higher stability of the latter is due to the double charge of the former. A large difference in the fluorescence quantum yields (Φ_F) between the alkali metal ions and the alkaline-earth metal ions would suggest that a stronger electrostatic interaction between the bivalent metal ions and the lone pair of the nitrogen atom of the aza-crown suppresses more efficiently the photoinduced electron transfer process.

Fig. 5 shows the fluorescence decay curves of PIAQ-Bu^t at 529 nm and PIAQ–AC at 515 nm in acetonitrile solution

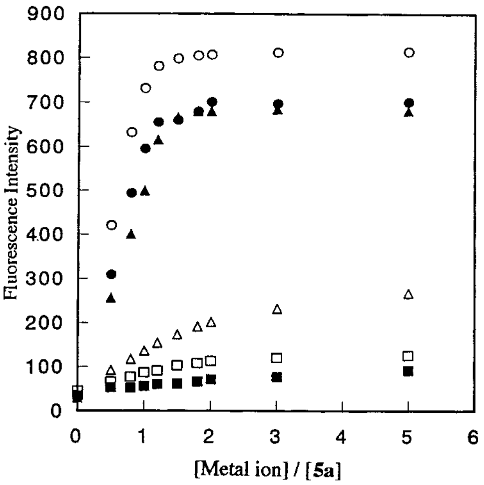


Fig. 3 Fluorescence intensity of **5a** *vs.* molar ratio of [metal salt]/[**5a**]. ([**5a**] = 2.5 × 10^{-5} mol dm^{-3}, λ_{em} = 515 nm, λ_{ex} = 400 nm); □: $LiClO_4$, ■: KSCN, △: NaSCN, ○: $Ca(SCN)_2$, ▲: $Mg(ClO_4)_2$, ●: $Ba(SCN)_2$.

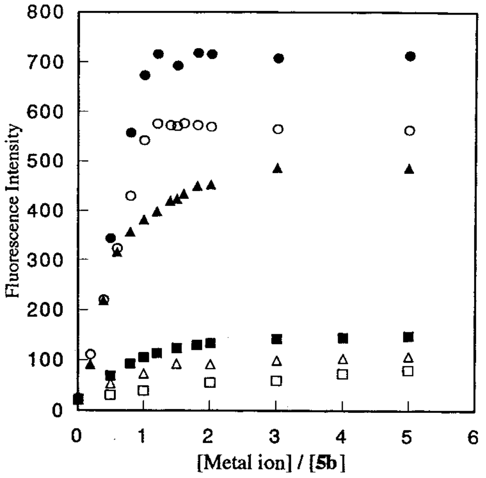


Fig. 4 Fluorescence intensity of **5b** *vs.* molar ratio of [metal salt]/[**5b**]. ([**5b**] = 2.5 × 10^{-5} mol dm^{-3}, λ_{em} = 515 nm, λ_{ex} = 400 nm); □: $LiClO_4$, ■: KSCN, △: NaSCN, ○: $Ca(SCN)_2$, ▲: $Mg(ClO_4)_2$, ●: $Ba(SCN)_2$.

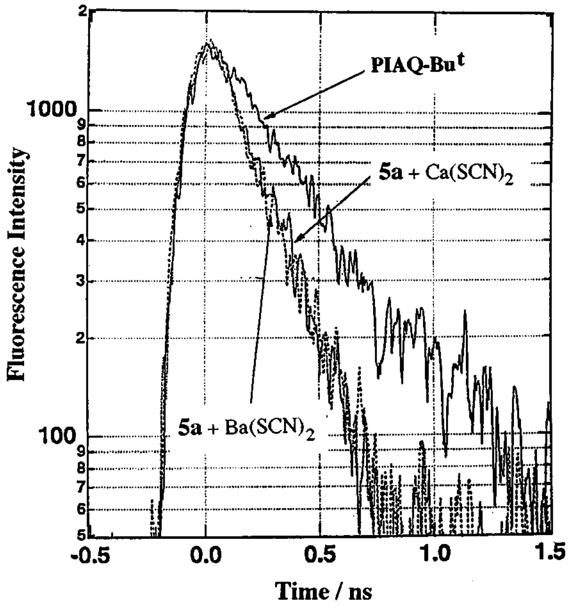


Fig. 5 Fluorescence decay curves of PIAQ-Bu^t at 529 nm and **5a** with metal salts at 515 nm in acetonitrile solutions, excited with a 400 nm femtosecond laser pulse ([PIAQ-Bu^t] = [**5a**] = 2.5 × 10^{-5} mol dm^{-3}, [$Ca(SCN)_2$] = [$Ba(SCN)_2$] = 1.25 × 10^{-4} mol dm^{-3}).

Table 1 Association constants (log *K*) and fluorescence quantum yields (Φ_F) of **5a** and **5b** and their complexes in acetonitrile

		Complexes					
	PIAQ–AC	Li^+	Na^+	K^+	Mg^{2+}	Ca^{2+}	Ba^{2+}
Ionic diameter/Å		1.36	1.96	2.66	1.32	1.98	2.68
5a[a]							
log *K*		4.62 ± 0.16	4.82 ± 0.04	4.32 ± 0.08	5.52 ± 0.29	6.51 ± 0.04	6.01 ± 0.12
$\Phi_F \times 10^2$	0.021	0.088	0.207	0.068	0.596	0.679	0.590
5b[a]							
log *K*		3.62 ± 0.30	4.96 ± 0.07	5.22 ± 0.02	5.78 ± 0.14	7.16 ± 0.02	7.24 ± 0.03
$\Phi_F \times 10^2$	0.019	0.085	0.100	0.131	0.439	0.507	0.601

[a] Cavity size[9] of the crown: aza-15-crown-5-ether (1.7–2.2 Å), aza-18-crown-6-ether (2.6–3.2 Å).

(2.5×10^{-5} mol dm^{-3}) under five times excess of metal salts, excited with a femtosecond laser at 400 nm. PIAQ-Bu^t was used as a model compound for PIAQ without AC. The decay for PIAQ-Bu^t is almost a single exponential with a lifetime of 420 ps. The fluorescence lifetime of PIAQ–AC in metal free conditions was too fast to be measured by our system. The fluorescence lifetimes of PIAQ–AC with Ca^{2+} and Ba^{2+} ions were estimated from Fig. 5 as 234 and 228 ps, respectively. These results strongly suggest that the fluorescence quenching is due to the photoinduced intramolecular electron transfer from AC to the excited PIAQ and that it is sensitively controlled by the electrostatic interactions between metal cations and the lone pair electrons in the aza-crown.

The time-resolved absorption spectra upon excitation with a femtosecond laser were measured in order to directly prove the above mechanism, the details of which will be reported elsewhere.[13] PIAQ-Bu^t exhibited transient absorption with a lifetime of 470 ps due to the excited singlet state. PIAQ–AC exhibited transient absorption of the excited singlet state with a lifetime of only 5.8 ps and a new absorption with a peak of 610 nm which was attributed to PIAQ anion radicals. From these results the fluorescent sensing of metal ions by PIAQ–AC due to the PET process was directly proved.

In conclusion, we have developed new fluorescent PET chemosensors based on a 2-phenylimidazo[5,4-*a*]anthraquinone (PIAQ) chromophore. The PIAQ chromophore is a good electron acceptor and exhibits absorption and emission bands in the visible region, which draw out favorable characteristics of the PIAQ–AC chemosensors. Marked fluorescence quenching by an intramolecular PET reaction from the AC to the excited PIAQ chromophore was directly proved. The changes in the association constants (log K) and fluorescence quantum yields (Φ_F) upon binding of metal ions to the aza-crown shown in Table 1 revealed that PIAQ–AC chemosensors can recognize the charge and the size of metal cations and precisely transform their information into the magnitude of the enhanced fluorescence. Thus, the PIAQ chromophore is a useful molecular part for designing new fluorescent chemosensors emitting visible signals.

Experimental

Mps were measured with a Yanaco micro melting point apparatus MP-500D and are uncorrected. ^{1}H NMR spectra were taken on a Hitachi Model R-90H spectrometer with tetramethylsilane (TMS) as an internal standard. IR spectra were recorded on a JASCO FT/IR-5300 spectrophotometer for samples in KBr pellet form. Elemental analyses were measured on a Perkin-Elmer 2400 II. Absorption spectra were measured using a JASCO U-best 30 spectrophotometer. Fluorescence spectra and quantum yields were measured with a JASCO FP-777 spectrophotometer. A solution of quinine sulfate in sulfuric acid (0.05 M) was used as the standard for quantum yield (Φ_F) measurements and taken to have $\Phi_F = 0.55$. Cyclic voltammetry was performed by means of a BAS CV-50W. A three-electrode system, containing of a glassy carbon working electrode and platinum wire counter electrode and a Ag/AgCl electrode as reference, was adopted. The electrolytic solvent was acetonitrile containing 0.1 mol dm^{-3} tetraethylammonium perchlorate (TEAP) as supporting electrolyte. Prior to measurements, all solutions were thoroughly degassed with argon for at least 20 min. The association constants (K) were obtained by a non-linear least-squares analysis reported by Bourson *et al.*[11] The fluorescence lifetimes were measured with an imaging spectrograph (Hamamatsu, C5094) and a streak scope (Hamamatsu, C2830) with a high speed streak unit (Hamamatsu, M2547). Acetonitrile for use in absorption and fluorescence spectroscopy or cyclic voltammetry was dried and distilled before use.

Synthesis of 1-amino-2-[4-(chloromethyl)benzoylamino]anthraquinone (3)

A solution of 4-(chloromethyl)benzoyl chloride (0.43 g, 4.62 mmol) in 1,4-dioxane (30 ml) was added dropwise to a solution of 1,2-diaminoanthraquinone (1.00 g, 4.2 mmol) and triethylamine (0.43 g, 4.2 mmol) in 1,4-dioxane (180 ml) with stirring at 60 °C. After being stirred for 7 h at 60 °C, the solvent was removed under reduced pressure, and the residue was washed with 50% aqueous ethanol, dried, and chromatographed on silica gel ($CHCl_3$–AcOEt = 3 : 1 as eluent) to give **3** (0.958 g, 60%). mp 256–257 °C. IR (KBr)/cm^{-1} 3422 (NH), 3304, 3229 (NH_2), 1655 (C=O), 1287, 718; ^{1}H NMR δ_H (DMSO-d_6) 4.85 (2H, s), 7.55–8.3 (12H, m), 9.93 (1H, b); (Found: C, 67.48; H, 3.86; N, 7.23. $C_{22}H_{15}N_2O_3Cl$ requires C, 67.61; H, 3.87; N, 7.17%).

Synthesis of 1-amino-2-[4-(aza-15-crown-5-ethermethyl)benzoylamino]anthraquinone (4a)

A mixture of the compound **3** (0.64 g, 1.54 mmol), 1-aza-15-crown-5-ether (0.405 g, 1.85 mmol), and triethylamine (0.47 g) in 1,4-dioxane (180 ml) was heated under reflux with stirring for 25 h. After the reaction, the solvent was removed under reduced pressure and the residue was extracted with CH_2Cl_2. The organic extract was washed with water and evaporated, the residue was chromatographed on silica gel ($CHCl_3$–AcOEt = 3 : 1 as eluent) and was further purified by recrystallization from 95% ethanol to give **4a** (0.58 g, 68%). mp 167–168 °C. IR (KBr)/cm^{-1} 3416 (NH), 3302 (NH_2), 2870 (CH_2), 1658 (C=O), 1283, 1105, 720; ^{1}H NMR δ_H ($CDCl_3$) 2.77 (4H, t), 3.5–3.8 (18H, m), 7.08 (2H, b), 7.45 (2H, d), 7.6–8.3 (9H, m); (Found: C, 66.77; H, 6.01; N, 7.17. $C_{32}H_{35}N_3O_7$ requires C, 67.00; H, 6.15; N, 7.33%).

Synthesis of 2-[4-(aza-15-crown-5-ethermethyl)phenyl]imidazo-[5,4-*a*]anthraquinone (5a)

A mixture of the compound **4a** (1.0 g, 1.74 mmol), NaOH (0.07 g, 1.75 mmol) in 95% ethanol (350 ml) was heated under reflux with stirring for 1.5 h. After cooling to room temperature, the reaction mixture was neutralized with aqueous HCl, and the solvent was evaporated, then the residue was washed with water. The crude product was chromatographed on silica gel (ethanol as eluent), and was further purified by recrystallization from 95% ethanol to give **5a** (0.420 g, 43%). mp 141–142 °C. IR (KBr)/cm^{-1} 3422 (NH), 2874 (CH_2), 1664 (C=O), 1296, 1092, 720; ^{1}H NMR δ_H ($CDCl_3$), 2.84 (4H, t), 3.5–3.9 (18H, m), 7.57 (2H, d), 7.7–7.9 (2H, m), 8.0–8.4 (6H, m), 11.25 (1H, b); λ_{max}(MeCN)/nm 405, ε_{max}/dm^3 mol^{-1} cm^{-1} 14,300; (Found: C, 68.93; H, 5.95; N, 7.47. $C_{32}H_{33}N_3O_6$ requires C, 69.17; H, 5.98; N, 7.56%).

Synthesis of 1-amino-2-[4-(aza-18-crown-6-ethermethyl)benzoylamino]anthraquinone (4b)

A mixture of the compound **3** (0.50 g, 1.28 mmol), 1-aza-18-crown-6 (0.404 g, 1.54 mmol) and triethylamine (0.389 g) in 1,4-dioxane (150 ml) was heated under reflux with stirring for 25 h. After the reaction, the solvent was removed under reduced pressure and the residue was extracted with CH_2Cl_2. The organic extract was washed with water and evaporated, the residue was chromatographed on silica gel ($CHCl_3$–AcOEt = 3 : 1 as eluent), and was further purified by recrystallization from 95% ethanol to give **4b** (0.506 g, 66%). mp 167–168 °C. IR (KBr)/cm^{-1} 3418 (NH), 3302 (NH_2), 2876 (CH_2), 1658 (C=O), 1281, 1109, 720; ^{1}H NMR δ_H ($CDCl_3$) 2.78 (4H, t), 3.5–3.8 (22H, m), 7.10 (2H, b), 7.46 (2H, d), 7.6–8.3 (9H, m); (Found: C, 65.83; H, 6.30; N, 6.74. $C_{34}H_{39}N_3O_8$ requires C, 66.11; H, 6.36; N, 6.80%).

Synthesis of 2-[4-(1,4,7,10,13,16-pentaoxaazacyclooctadecin-16-yl)phenyl]imidazo[5,4-*a*]anthraquinone (5b)

A mixture of the compound **4b** (0.704 g, 1.14 mmol), NaOH (0.06 g, 1.15 mmol) in 95% ethanol (250 ml) was heated under reflux with stirring for 1.5 h. After cooling to room temperature, the reaction mixture was neutralized with aqueous HCl, and the solvent was evaporated, then the residue was washed with water. The crude product was chromatographed on silica gel (ethanol as eluent), and was further purified by recrystallization from 95% ethanol to give **5b** (0.325 g, 48%). mp 143–144 °C. IR (KBr)/cm^{-1} 3435 (NH), 2870 (CH_2), 1666 (C=O), 1296, 1109, 716; ^{1}H NMR δ_H ($CDCl_3$) 2.84 (4H, t), 3.5–3.9 (22H, m), 7.57 (2H, d), 7.7–7.9 (2H, m), 8.0–8.4 (6H, m), 11.25 (1H, b); λ_{max}(MeCN)/nm 405, ε_{max}/dm^3 mol^{-1} cm^{-1} 14,500; (Found: C, 67.86; H, 6.19; N, 6.92. $C_{34}H_{37}N_3O_7$ requires C, 68.10; H, 6.22; N, 7.01%).

Synthesis of 2-(4-*tert*-butylphenyl)imidazo[5,4-*a*]anthraquinone (PIAQ-Bu^t)

4-*tert*-Butylbenzoyl chloride (1.69 g, 8.60 mmol) was added dropwise to a solution of 1,2-diaminoanthraquinone (2.00 g, 8.40 mmol) and Na_2CO_3 (0.89 g, 8.40 mmol) in pyridine (30 ml) with stirring. After being stirred for 1 h at 60 °C, the solvent was evaporated and the residue was washed with hot water and dried. The resulting orange powder was dissolved in pyridine (60 ml), and NaOH (0.40 g, 10.0 mmol) dissolved in water (10 ml) was added to the solution. After the mixture had been stirred for 1 h at 70 °C, cooled to room temperature, neutralized with aqueous HCl, and the solvent was evaporated, the residue was washed with water. The crude product was chromatographed on silica gel ($CHCl_3$–AcOEt = 9 : 1 as eluent), and was further purified by recrystallization from ethyl acetate to give **PIAQ-Bu^t** (2.94 g, 92%). mp 245–245.5 °C. IR (KBr)/cm^{-1} 3432 (NH), 2961, 1665 (C=O); ^{1}H NMR δ_H ($CDCl_3$), 1.39 (9H, s), 7.5–7.8 (4H, m), 7.9–8.3 (6H, m), 11.19 (1H, bs); λ_{max} (MeCN)/nm 403, ε_{max}/dm^3 mol^{-1} cm^{-1} 15,300; (Found: C, 79.21; H, 5.31; N, 7.15. $C_{25}H_{20}N_2O_2$ requires C, 78.93; H, 5.30; N, 7.36%).

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