RSC Advances

PAPER

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Cite this: *RSC Adv.*, 2021, **11**, 24217

Color-tunable arylaminoanthraquinone dyes through hydrogen-bond-assisted charge transfer interaction†

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Received 22nd May 2021
Accepted 5th July 2021

DOI: 10.1039/d1ra03985g

rsc.li/rsc-advances

We prepared a series of arylaminoanthraquinone derivatives, including those with electron-accepting sulfone units and/or with electron-donating dialkylamino units. A color-tunable anthraquinone library that reached into the NIR region could be prepared through the precise control of frontier orbitals. Fine color-tuning was achieved through proper selection and positioning of the substituents. Effective intramolecular hydrogen-bond-assisted charge transfer interaction between electron-donating aniline/*p*-phenylenediamine and electron-accepting anthraquinone substructures induced a significant bathochromic shift of anthraquinone. The number and position of the substituents and the molecular conformation also significantly contributed to determining photophysical properties.

Introduction

Recently, π-conjugated molecules with a small HOMO–LUMO gap that absorb long-wavelength light, including near-infrared (NIR) light have attracted attention[1–6] due to their potential for use in optoelectronic devices,[5,7–11] optical devices,[1,6,12] and medical applications.[13–15] There are several approaches to develop such molecules, including the expansion of π-conjugation and the introduction of an open-shell biradical unit in π-conjugation. A variety of long-wavelength absorbing dyes have been developed with these strategies, including porphyrin/phthalocyanine derivatives,[1] including their conjugated array,[16–19] polymethine/cyanine derivatives,[1,20–25] boron-dipyrromethene (BODIPY) derivatives,[26,27] polyacenes,[28–31] zethrenes derivatives,[32–35] and indenofluorene derivatives.[36–47] However, these compounds often suffer from difficult synthesis and low solubility in common organic solvents.

The introduction of intramolecular charge transfer (CT) interaction between an electron-donating group (D) and an electron-accepting group (A) in a π conjugated unit is also widely used to develop long-wavelength absorbing dyes.[1–4,48–50] While a variety of long-wavelength absorbing dyes have been developed, quinone and its π-extended derivatives have been especially used for this purpose because of their strong electron-accepting properties.[1] Especially, anthraquinone has been used due to its easy functionalization.[51] Several commercially available dyes have an anthraquinone skeleton, such as the disperse blues. Some disperse blues contain electron-donating aniline/*p*-phenylenediamine unit(s) fused with an electron-accepting anthraquinone core. Since the degree of intramolecular CT interaction can be modulated through the electron-donating/accepting properties of D and A, this skeleton could serve as a color-tunable long-wavelength absorbing dye. However, little is known about long-wavelength absorbing dyes based on a aminoanthraquinone scaffold.

We previously studied the photophysical and electrochemical properties of arylsulfonamide-substituted anthraquinones **3**, **9**, **14**, and **20**.[52,53] Thanks to effective intramolecular N–H···O=C hydrogen bonds at the *peri*-position of anthraquinone through fixation of the conformation by bulky terminal substituents, the electron-accepting properties of the anthraquinone units significantly increased, which induced a significant bathochromic shift in UV-Vis spectra thanks to hydrogen-bond-assisted CT interaction (Fig. 1a).[54] We also revealed that *N*-methylation of these derivatives induced a drastic change in conformation to completely suppress this intramolecular CT interaction.[55]

In this work, we systematically prepared arylaminoanthraquinones and investigated their photophysical and electrochemical properties (Fig. 1b). Thanks to hydrogen-bond-assisted CT interaction, these compounds showed significant bathochromic absorption compared to anthraquinone. Their photophysical properties could be systematically modulated by the introduction of electron-donating dialkylamino groups at peripheral phenyl groups or the insertion of electron-accepting sulfone groups between an amino unit and phenyl group. As

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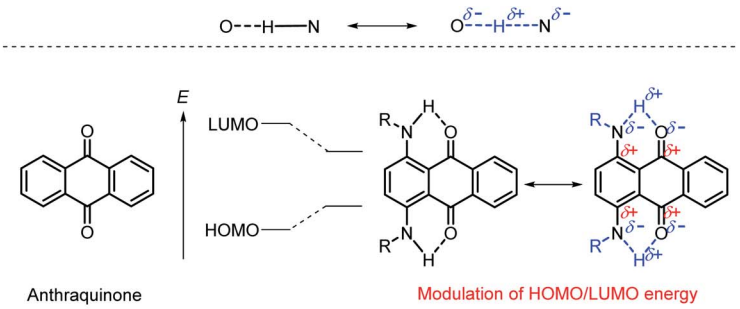
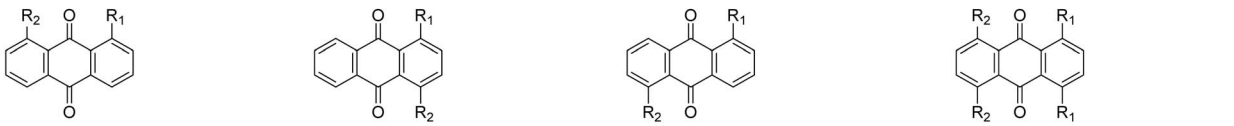
† Electronic supplementary information (ESI) available: ORTEP drawing of **22**. Cyclic voltammograms of **1–23** classified according to the substituent. HOMO and LUMO of **1–6**, **11**, **13–23**. Copies of the ^{1}H and ^{13}C NMR spectra of new compounds. Cartesian coordinates for the optimized structures of **1–23**. CCDC 2063387. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/d1ra03985g





1: $R_1 = R_2 =$ 4-MeC_6H_4NH
2: $R_1 = R_2 =$ 4-$Me_2NC_6H_4NH$
3: $R_1 = R_2 =$ 4-$MeC_6H_4SO_2NH$
4: $R_1 = R_2 =$ 4-$Me_2NC_6H_4SO_2NH$
5: $R_1 =$ 4-$Me_2NC_6H_4NH$, R_2 = Cl
6: $R_1 = R_2 =$ 4-$MeC_6H_4SO_2NMe$

7: $R_1 = R_2 =$ 4-MeC_6H_4NH
8: $R_1 = R_2 =$ 4-$Me_2NC_6H_4NH$
9: $R_1 = R_2 =$ 4-$MeC_6H_4SO_2NH$
10: $R_1 = R_2 =$ 4-$Me_2NC_6H_4SO_2NH$
11: $R_1 =$ 4-$Me_2NC_6H_4NH$, R_2 = Cl
12: $R_1 = R_2 =$ 4-$MeC_6H_4SO_2NMe$

13: $R_1 = R_2 =$ 4-$tBuC_6H_4NH$
14: $R_1 = R_2 =$ 4-$tBuC_6H_4SO_2NH$
15: $R_1 = R_2 =$ 4-$Bu_2NC_6H_4SO_2NH$
16: $R_1 =$ 4-$Me_2NC_6H_4NH$, R_2 = Cl
17: $R_1 =$ 4-$Me_2NC_6H_4SO_2NH$, R_2 = Cl
18: $R_1 = R_2 =$ 4-$tBuC_6H_4SO_2NMe$

19: $R_1 = R_2 =$ 4-$tBuC_6H_4NH$
20: $R_1 = R_2 =$ 4-$tBuC_6H_4SO_2NH$
21: $R_1 = R_2 =$ 4-$Hex_2NC_6H_4SO_2NH$
22: $R_1 =$ 4-$Bu_2NC_6H_4SO_2NH$, $R_2 = NH_2$
23: $R_1 = R_2 =$ 4-$tBuC_6H_4SO_2NMe$

Fig. 1 (a) Hydrogen-bond-assisted CT interaction in aminoanthraquinone derivatives with bulky aryl substituents.[52] (b) Chemical structure of aminoanthraquinones described in this manuscript.

a result, color-tunable aminoanthraquinone dyes that reached into the NIR region could be prepared.

Results and discussion

Preparation of aminoanthraquinones with electron-donating/accepting units

We prepared a series of aminoanthraquinones with different electron-donating/accepting units. Fig. 1 shows the molecular structures of aminoanthraquinones described in this manuscript. Since our previous study revealed that a bulky aryl substituent at the peripheral position of aminoanthraquinones worked effectively to form N–H···O=C hydrogen bonds, we adopted this strategy to maximize hydrogen-bond-assisted CT interaction. We selected a dialkylamino unit on terminal phenyl groups as an electron-donating unit and a sulfone unit between aminoanthraquinone and terminal phenyl group as an electron-accepting unit. The positional and numerical effects of substituents on the photophysical and electrochemical properties should also be considered, since phenylenediamine and its derivatives have been reported to be strong electron donors. Based on this strategy, we synthesized 23 kinds of aminoanthraquinones for this purpose, including those we previously reported[52,55] and those in the literature (**1**, **7**, **13**, **19**).[56–59] A substituent was introduced at the 1,4-, 1,5-, 1,8- or 1,4,5,8-positions in each compound. Terminal methyl, butyl, *tert*-butyl and hexyl groups were introduced to improve their solubility.

Fig. 2 summarizes the synthesis of **1–23** with/without electron-donating/accepting units. Most of the compounds were synthesized through a Buchwald–Hartwig cross-coupling reaction[60–63] or Ullmann coupling reaction[64] between the corresponding chloroanthraquinone and arylamine/arylsulfonamide, respectively. The reaction of alkylphenylamine and alkylphenylsulfonamide without terminal electron-donating alkylamino groups proceeded smoothly to give the corresponding arylamino derivatives (**1**, **13**, **19**)[58,59] and arylsulfonamide derivatives (**3**, **9**, **14**, **20**) in good yields. In the case of 1,5-disubstituted (**13**, **14**) and 1,4,5,8-tetrasubstituted derivatives (**19**, **20**), a terminal *tert*-butyl group was necessary to increase the solubility to accomplish the reaction. In the reactions of 1,4- and 1,8-dichloroanthraquinone with stronger electron-donating *N*,*N*-dimethyl-1,4-phenylenediamine, the reaction did not proceed completely and gave both the desired disubstituted derivatives (**2**, **8**) and monosubstituted derivatives with unreacted chlorine atom (**5**, **11**). If we consider that a significant amount of unreacted monochloro derivative was recovered only in the reaction with phenylenediamine derivatives, this could be accounted for by suppression of the reactivity of monochloro intermediate with Pd catalyst due to the decreased electron-withdrawing properties of arylanthraquinones by introduction of an electron-donating dimethylaminophenyl unit. In the reaction of 1,5-dichloroanthraquinone, only monosubstituted derivative (**16**) was obtained, due to the relatively limited solubility of 1,5-disubstituted derivatives (see above), in addition to limited reactivity. In the reaction with *N*,*N*-dimethylaminophenylsulfonamide,[65] only the corresponding 1,4- and 1,8-substituted derivatives **4**, **10** were obtained in moderate yields, whereas the 1,5- and 1,4,5,8-substituted derivatives were not obtained under the same reaction conditions. If we consider the decreased electron-donating nature of the terminal NH_2 group suitable for the Buchwald–Hartwig cross-coupling reaction due to the neighboring electron-accepting sulfone unit, this limited reactivity was due to the limited solubility of these derivatives, rather than the reactivity. To obtain 1,5- and 1,4,5,8-substituted derivatives, we planned to introduce long alkyl chains (butyl groups for **15** and

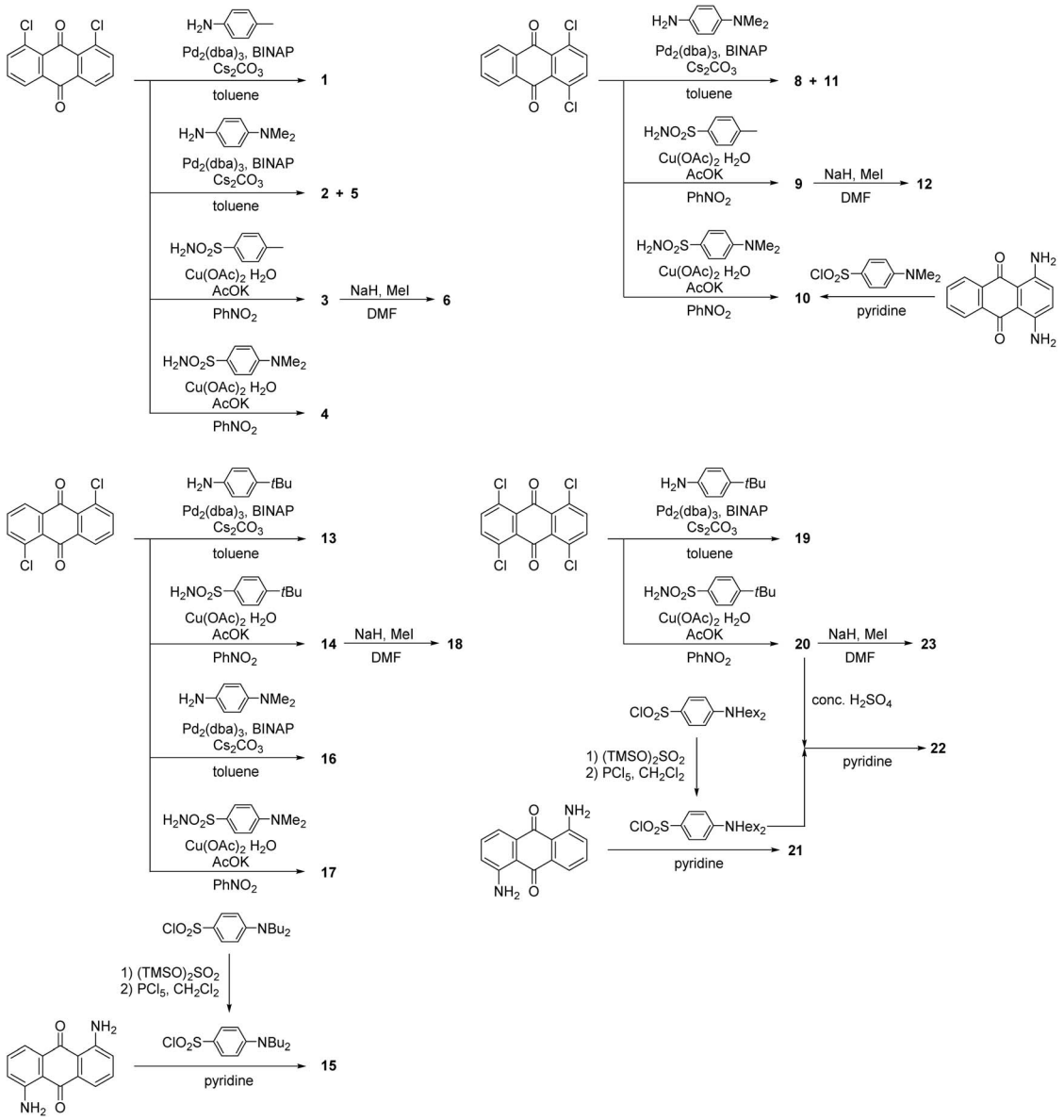


Fig. 2 Synthesis of **1–23**.

hexyl groups for **21**) to a terminal amino group, instead of a methyl group. To achieve this, we changed the synthetic strategy and planned to react the corresponding aminoanthraquinone with 4-(dialkylamino)benzene sulfonyl chloride. 4-(Dibutylamino) benzenesulfonyl chloride and (dihexylamino)benzenesulfonyl chloride were newly prepared from dibutylamine and dihexylamine, respectively, by the reaction with $(TMSO)_2SO_2$ followed by PCl_5. The reaction of the corresponding commercially available aminoanthraquinone with 4-(dialkylamino)benzene sulfonyl chloride in pyridine proceeded smoothly to give the desired dialkylaminophenylsulfonamide-substituted anthraquinones **15** and **21**. When we tried the reaction between (dibutylamino)benzenesulfonyl chloride and 1,4,5,8-tetraaminoanthraquinone, prepared in-house by hydrolysis of **20**, we unexpectedly obtained partly reacted 1,4-disubstituted-5,8-diaminoanthraquinone **22**, although we could not clarify the mechanism or selectivity. The structure of **22** was rigorously characterized by single-crystal X-ray structural analysis (Fig. S1 in ESI†). *N*-Methylation of arylsulfonamide derivatives **3**, **9**, **14**, **20** gave the corresponding *N*-methylated derivatives (**6**, **12**, **18**, **23**). All newly synthesized compounds were characterized by ^1H and ^{13}C NMR, IR and HR-MS spectroscopy and elemental analyses.

Photophysical properties

We measured UV-Vis/NIR spectra of **1–23** to investigate the effect of the electron-donating/accepting substituent and the positional/numerical effects of the substituents. Fig. 3 and 4 show the UV-Vis spectra in CH_2Cl_2 classified according to the substitution position and the substituent, respectively, and Table 1 summarizes the photophysical and electrochemical properties of **1–23**, in addition to their theoretical HOMO and

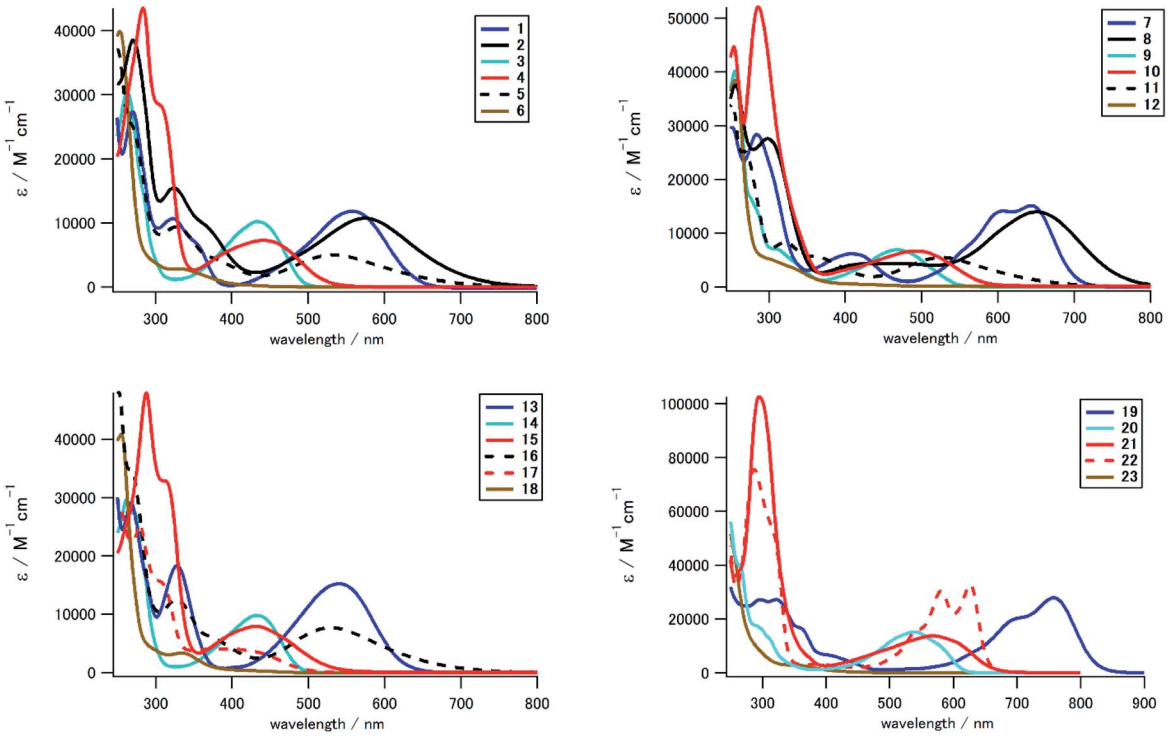


Fig. 3 UV-Vis spectra of **1–23** in CH_2Cl_2 classified according to the substitution position. The color was determined by the introduced substituent. The dotted line indicates monochloro-monosubstituted derivatives or diamino-disubstituted derivative.

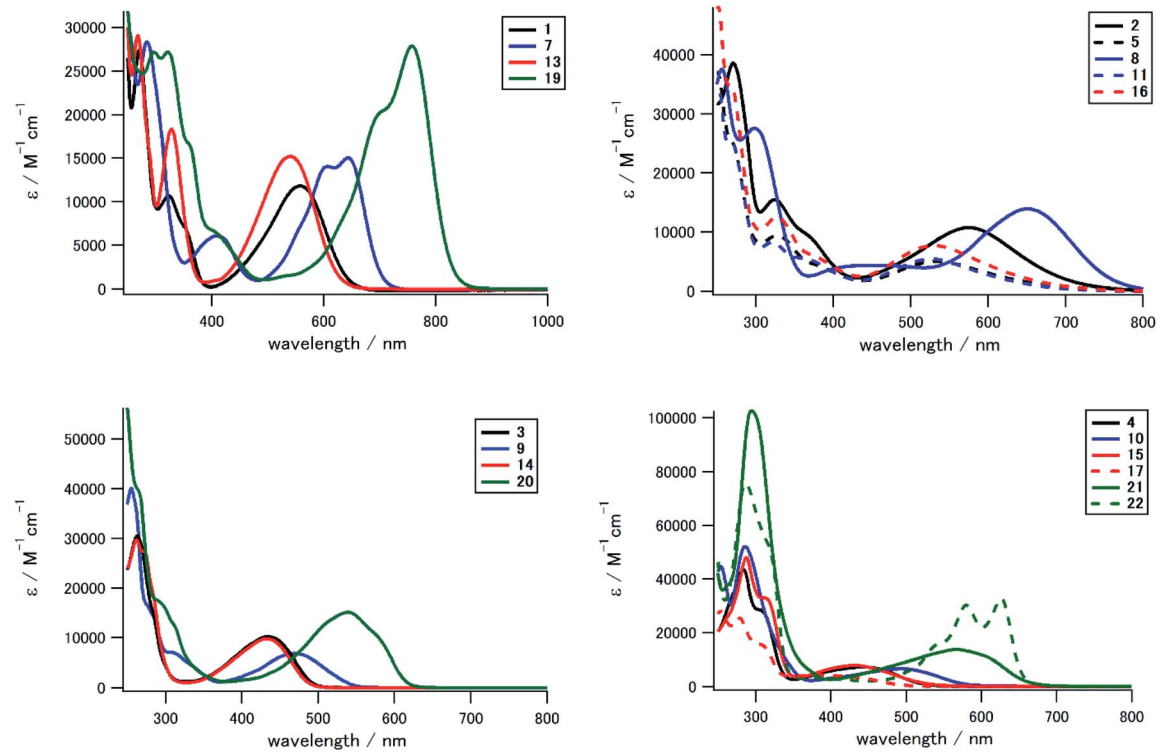


Fig. 4 UV-Vis spectra of **1–22** in CH_2Cl_2 classified according to the substituent. The color was determined by the position of the introduced substituent. The dotted line indicates monochloro-monosubstituted derivatives or diamino-disubstituted derivative.

Table 1 Photophysical and electrochemical properties, calculated HOMO–LUMO energy and the lowest-energy absorption peak

Compd	λ_{max}[a]	ε[b]	λ_{end}[c]	E_{pa}[d]	E_{pc}[d]	HOMO[e]	LUMO[e]	Abs. calc.[f]
1	559	11 800	654	1.61[h]	−0.92,[i] −1.27[i]	−5.19	−2.59	577
2	576	10 700	755	0.83[h]	−0.98,[i] −1.37[i]	−4.65	−2.33	651
3	434	10 200	498	NA[k]	−0.52,[i] −0.92[i]	−6.41	−3.15	463
4	442	7200	535	1.43[h]	−0.55,[i] −0.94[i]	−5.75	−2.91	512
5	534	5000	707	0.73[i]	−0.87,[i] −1.25[i]	−4.93	−2.64	651
6	331	2800	403	NA[k]	−0.87,[i] −1.36[i]	−6.30	−2.72	472[l]
7	645	15 000	718	1.01, 1.46[i]	−0.95,[i] −1.28[i]	−4.82	−2.54	609
8	652	13 900	795	0.77[h,j]	−1.00,[i] −1.30[i]	−4.36	−2.25	659
9	468	6800	547	NA[k]	−0.60[i]	−6.09	−3.18	495
10	494	6600	592	1.42[h]	−0.52,[i] −0.65[i]	−5.53	−2.91	557
11	529	5400	693	0.77[h]	−0.87,[i] −1.28[i]	−5.02	−2.62	615
12	337	3100[g]	410	NA[k]	−0.82,[i] −1.29[i]	−6.33	−2.74	481[l]
13	539	15 200	646	1.40[h]	−0.89,[i] −1.26[i]	−5.25	−2.59	555
14	432	9800	494	NA[k]	−0.53[i]	−6.44	−3.15	449
15	432	7900	547	1.46[i]	−0.61[i]	−5.67	−2.95	534[l]
16	530	7700	721	0.77[i]	−0.87,[i] −1.30[i]	−4.96	−2.64	634
17	418	3900[g]	498	1.24[h]	−0.64,[i] −0.91[i]	−5.74	−2.98	526[l]
18	333	3400	400	NA[k]	−0.83,[i] −1.36[i]	−2.82	−6.28	495[l]
19	758	27 900	855	0.60,[i] 1.02[h]	−0.97,[i] −1.22[i]	−4.40	−2.44	726
20	539	15 100	624	NA[k]	−0.21,[i] −0.54[i]	−5.96	−3.37	563
21	568	13 700	686	1.46[h]	−0.35,[i] −0.66[i]	−5.44	−2.98	593
22	626	32 700	677	0.97,[i] 1.38[h]	−0.89[i,j]	−5.05	−2.61	573
23	355	2800[g]	431	NA[k]	−0.92,[i] −1.51[i]	−6.20	−2.62	480[l]

[a] nm. Measured in CH_2Cl_2. [b] M^{-1} cm^{-1}. [c] nm. Shortest wavelength with ε < 500. [d] V *vs.* Ag/AgCl. Measured in CH_2Cl_2 containing Bu_4NBF_4. [e] eV. Calculated at the B3LYP/6-31G(d) level. [f] Theoretical HOMO–LUMO transition energy in nm. Calculated at the B3LYP/cc-pVDZ level. [g] Shoulder. [h] Irreversible. [i] Reversible. [j] Broad. [k] Not observed. [l] Forbidden transition (oscillator strength < 0.05).

LUMO energies and the lowest-energy absorption peak. As seen in the UV-Vis spectra and Fig. 5, we could prepare a color-tunable anthraquinone library through precise control of the frontier orbital. Fine color-tuning was achieved through proper selection and positioning of the substituents. As shown in Fig. 3, the photophysical properties of aminoanthraquinone could be greatly modulated by selecting the substituents. In the case of 1,8-disubstituted anthraquinones, that with a tolylamino group (**1**) showed bathochromic absorption at λ_{max} 559 nm, which is red-shifted by 233 nm compared to that for anthraquinone. This could be accounted for by effective intramolecular CT interaction between the electron-donating aniline/*p*-phenylenediamine substructure and the electron-accepting anthraquinone substructure (see below). Introduction of an electron-accepting sulfone unit between amino and aryl units significantly modulated the photophysical properties. Tolylsulfonamide-substituted anthraquinone **3** showed an absorption peak at 434 nm, which is blue-shifted by 125 nm compared to that of **1**, due to a larger decrease in the HOMO energy (**1**: −5.19 eV; 3: −6.41 eV) than that in LUMO energy (**1**: −2.59 eV; **3**: −3.15 eV) (Table 1). Substitution of a terminal alkyl group with an electron-donating dialkylamino unit also affected the optical properties, which was suitable for fine tuning. Substitution of the terminal methyl groups of **1** and **3** with dimethylamino groups (**2** and **4**, respectively) induced a slight red shift of the absorption peak (λ_{max}: 17 and 10 nm, respectively) and a moderate-to-large red shift of the absorption end (λ_{end}: 95 and 37 nm, respectively). This red shift is accounted for by a increase in the HOMO energy (**1**: −5.19 eV; **2**: −4.65 eV/**3**: −6.41 eV; **4**: −5.75 eV, Table 1). A similar tendency of the substituent effect was observed for other positional isomers. Halogen substituents also significantly contributed to determine the photophysical properties. For example, mono-substituted derivatives **5**, **11**, and **16** with dialkylphenylamino groups showed a hypochromic shift of *ca.* 40 nm compared to **2** with the same aniline substructure. While arylsulfonamide derivatives (**3**, **9**, **14**, **20**) showed unique fluorescence even with

Fig. 5 Photographic demonstration of fine color-tuning with aminoanthraquinone-based dyes with **1**–**23** (arranged by compound number from the left).

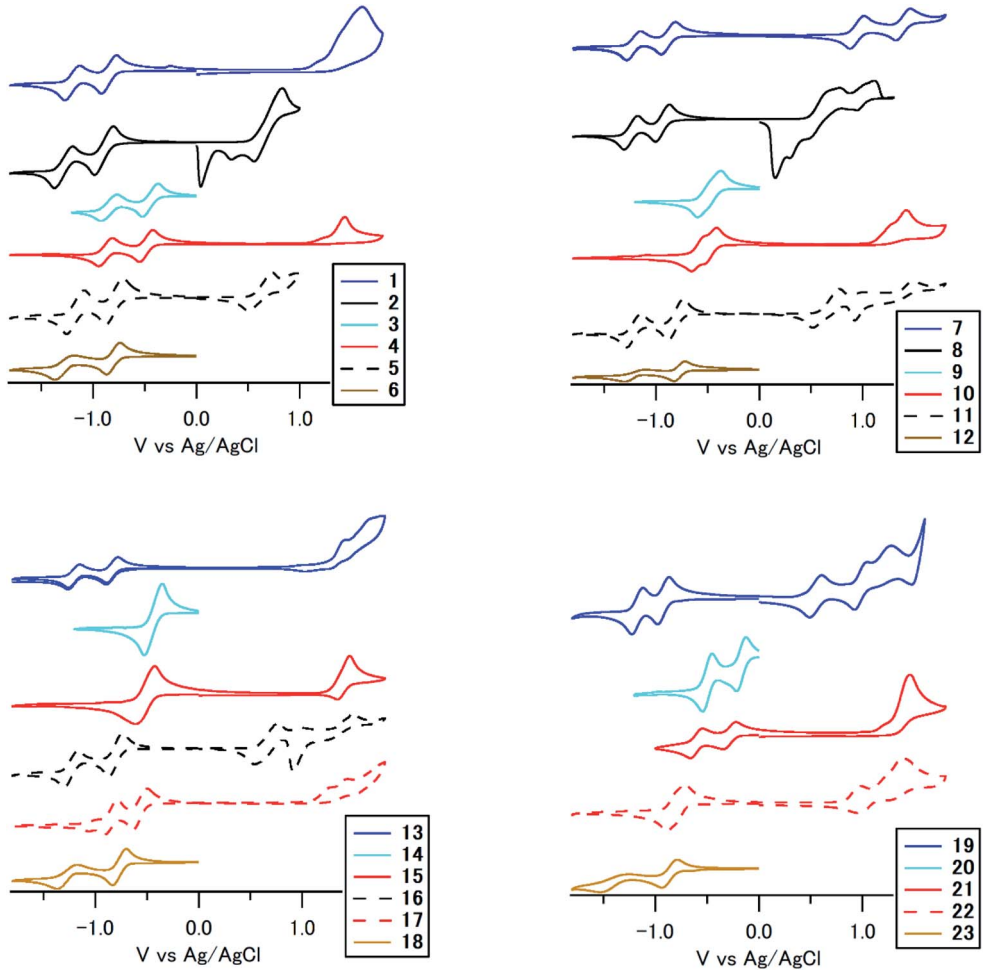


Fig. 6 Cyclic voltammograms of **1–23** measured in CH_2Cl_2 classified according to the substitution position. The color was determined by the introduced substituent. The dotted line indicates monochloro-monosubstituted derivatives or diamino-disubstituted derivative.

a non-fluorescent anthraquinone core,[52] other derivatives did not exhibit fluorescence.

In addition to the kinds of substituents, the position and number of the substituents also significantly affected the photophysical properties of these derivatives, as summarized in Fig. 4. The absorption peak/end were significantly different for positional isomers with the same substituents. For example, for alkylphenylamino derivatives (**1**, **7**, **13**, **19**), the absorption peak differs by *ca.* 220 nm (**13**: 539 nm, **19**: 758 nm). This large difference in photophysical properties could be understood in terms of the different electron-donating natures of the aniline/*p*-phenylenediamine substructure. HOMO energies of **7** (−4.82 eV) and **19** (−4.40 eV) with stronger electron-donating *p*-phenylenediamine substructure are higher than those of **1** (−5.19 eV) and **13** (−5.25 eV) with weaker electron-donating aniline substructure. The 1,4-disubstituted and 1,4,5,8-tetrasubstituted derivatives with a stronger electron-donating *p*-phenylenediamine substructure contributed to stronger intramolecular CT interaction.

Tetrasubstituted derivatives have longer absorption among the derivatives with same substituents. For example, the absorption of tetrasubstituted derivative **19** with alkylphenylamino groups showed a large red shift of *ca.* 110 nm compared to that of the corresponding 1,4-disubstituted **7** with the same *p*-phenylenediamine electron-donating groups. DFT calculation indicates that the orbital degeneracy of electron-donating substructure units contributed to increase the HOMO energy (**19**: −4.40 eV, **7**: −4.82 eV, Fig. S6†). As a result, significant red shift occurred in tetrasubstituted derivatives.

In addition, *N*-methylation induced a drastic hypochromic shift due to the change in the conformation of a terminal arylamino/arylsulfonamide group.[55] For example, the absorption peak at the longest wavelength for *N*-methylated tetrasubstituted derivative **23** showed a blue shift of 190 nm compared to that of the corresponding N–H derivative **20**. *N*-Methylation at the congested *peri*-position of the anthraquinone unit induced a drastic change in conformation from a coplanar arrangement to an orthogonal arrangement between the anthraquinone scaffold and arylsulfonamide substituents. This drastic structural change significantly affected its LUMO energy and HOMO structure to suppress the CT interaction between the anthraquinone π unit and sulfonamide substituents. We could prepare a color-tunable anthraquinone dye library (λ_{max}: 331–758 nm, λ_{end}: 400–855 nm) that extended into the NIR region.

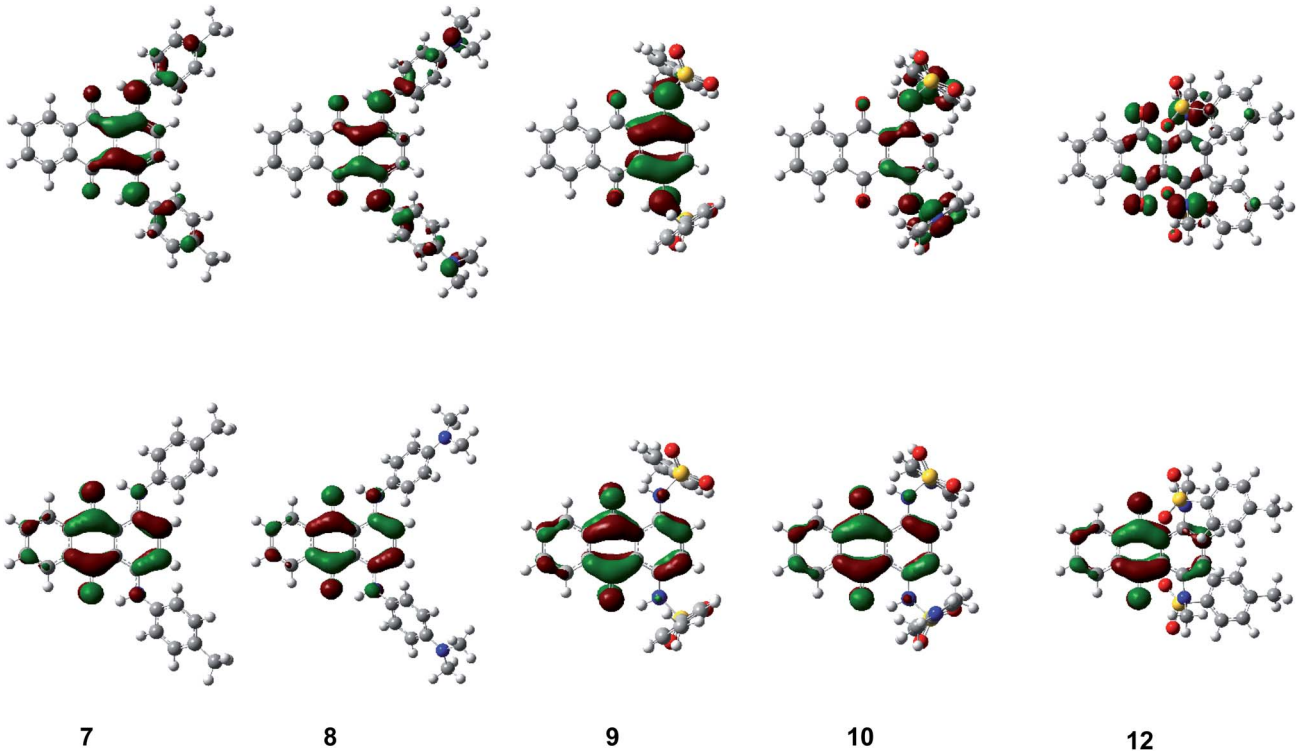


Fig. 7 HOMO (top) and LUMO (bottom) of 1,4-disubstituted anthraquinones **7–10** and **12**.

Electrochemical properties and DFT calculations

To understand the huge differences in absorption among **1–23**, we performed cyclic voltammetry and DFT calculations. Fig. 6 and S2 (ESI†) summarize the results according to the substitution position and the substituent, respectively. The compounds show reversible reduction peaks and irreversible (some reversible) oxidation peaks at −0.52 to −1.00 V (E_{pc1}), −0.54 to −1.51 V (E_{pc2}) and 0.60–1.61 V (E_{pa1}) *vs.* Ag/AgCl, respectively, which is accounted for by reduction of the electron-accepting anthraquinone core and oxidation of the electron-donating terminal arylamino/arylsulfonamide group. In the reduction process, compounds with arylsulfonamide substituents (**3**, **4**, **9**, **10**, **14**, **15**, **20**, **21**) showed a significant anodic shift (E_{pc1}: −0.21 to −0.61 V) compared to other compounds (−0.82 to −1.00 V), which is accounted for by an effective intramolecular N–H···O=C hydrogen bonding effect between electron-donating arylsulfonamide groups and the electron-accepting anthraquinone core.[52] On the other hand, the reduction potential of other compounds was almost equal to that of anthraquinone, which indicates that an intramolecular N–H···O=C hydrogen bonding effect did not work effectively for arylaminoanthraquinones without an electron-accepting sulfone unit. In the oxidation process, its potentials were mainly governed by the electron-donating unit. For example, compounds with stronger electron-donating dialkylaminophenylamino units showed a significant cathodic shift of the oxidation peak. 1,4-Disubstituted and 1,8-tetrasubstituted derivatives with stronger *p*-phenylenediamine donor units are stronger electron donors than 1,5- and 1,8-disubstituted derivatives with weaker aniline donor units.

The theoretically calculated HOMO–LUMO energy and simulated absorption by DFT calculations well reproduced the trend in the experimental results. Fig. 7 and S3–S6 (ESI†) show the HOMO and LUMO of 1,4-disubstituted derivatives **7–10**, **12** and other compounds **1–6**, **11**, **13–23** for their optimized structures. N–H units faced a carbonyl unit to form intramolecular hydrogen bonding interaction in all non-*N*-methylated derivatives. HOMO was located on an electron-donating *p*-phenylenediamine/aniline substructure whereas LUMO was located on an electron-accepting central *p*-quinone substructure. Since HOMO/LUMO were both co-located on the same π-conjugated plane, transition-allowed intramolecular CT occurred effectively to induce a significant bathochromic shift depending on the electron-donating unit. Since similar intramolecular hydrogen bonding interaction was observed in all N–H compounds, intramolecular N–H···O=C hydrogen bonding contributed to their frontier orbitals. LUMO was located on N–H nitrogen atoms in all N–H compounds, in addition to an anthraquinone unit, which decreased its energy through intramolecular N–H···O=C hydrogen bonding, as observed in their cyclic voltammetry measurement, which resulted in a significant bathochromic shift in the UV-Vis spectra (hydrogen-bond-assisted CT interaction). The degree of modulation of LUMO energy through intramolecular hydrogen bonding interaction differs between the compounds depending on the substituents. The LUMO energies of sulfonamide derivatives were more reduced through N–H···O=C

hydrogen bonding, as demonstrated by comparison with the corresponding N–Me derivatives without intramolecular hydrogen bonding interaction. On the other hand, the LUMO energies of other derivatives with arylamino groups was less influenced through intramolecular N–H···O=C hydrogen bonding, which could be accounted for by the different orbital contributions of frontier orbitals between compounds with/without an electron-accepting sulfone unit. *N*-Methylation of sulfonamide derivatives also affected the LUMO energy and absorption spectra, since it induced a drastic structural change from a coplanar arrangement to an orthogonal relationship between the anthraquinone scaffold and arylsulfonamide substituents, which suppresses intramolecular N–H···O=C hydrogen bonding and forbits effective HOMO–LUMO transition.

Conclusion

We prepared a series of arylaminoanthraquinone derivatives including those with electron-accepting sulfone units and electron-donating dialkylamino units. As demonstrated in UV-Vis spectra, we could prepare a color-tunable anthraquinone library that reached into the NIR region through the precise control of frontier orbitals. Fine color-tuning was achieved through proper selection and positioning of the substituents. Effective intramolecular hydrogen-bond-assisted CT interaction between electron-donating aniline/*p*-phenylenediamine and electron-accepting anthraquinone substructures induced a significant bathochromic shift for the anthraquinone. The introduction of an electron-accepting sulfone unit between amino and aryl units significantly modulated the photophysical properties. Substitution of a terminal alkyl group with an electron-donating dialkylamino unit also affected the optical properties, which is suitable for fine color-tuning. The number and position of the substituent also significantly contributed to determine the photophysical properties. Especially, tetrasubstituted derivatives showed a larger red shift compared to other derivatives due to the orbital degeneracy of stronger electron-donating *p*-phenylenediamine substructures. The change in conformation induced by *N*-methylation at the congested *peri*-position of the anthraquinone unit suppressed the interaction between the anthraquinone π unit and sulfonamide substituents to induce a significant hypochromic shift.

Experimental section

General methods

Commercially available reagents and solvents were used without further purification. NMR spectra were measured in $CDCl_3$ on a Bruker Avance III 400 or a Bruker Avance III 500 NMR spectrometer. Chemical shifts (δ) in ppm were referenced to an internal standard of tetramethylsilane (^{1}H) or residual nondeuterated solvent (^{13}C: 77.0 ppm for $CDCl_3$). Mass spectra were obtained in EI or FAB mode with a JMS-700 mass spectrometer at the NMR and MS Laboratory, Graduate School of Agriculture, Tohoku University. Infrared (IR, 400–4000 cm^{-1}) spectra were measured on a KBr pellet with a Thermo Scientific NICOLET 6700 FT-IR spectrometer with a resolution of 4 cm^{-1}. UV-Vis spectra were measured in CH_2Cl_2 (for spectrochemical analysis). Cyclic voltammetry was performed in dry CH_2Cl_2 containing 0.1 M Bu_4NBF_4 with a scan rate of 100 mV s^{-1}. A glassy carbon electrode, Pt electrode and Ag/AgCl electrode were used as the working, counter, and reference electrodes, respectively.

Single-crystal X-ray structure analysis

Crystallographic data were collected using a diffractometer equipped with a rotating anode fitted with a multilayer confocal optic using Cu-K$_\alpha$ (λ = 1.54187 Å) radiation. Structure refinements were carried out using the full-matrix least-squares method on F^2. Calculations were performed using the Crystal Structure and SHELEX software packages.[66] Parameters were refined using anisotropic temperature factors except for the hydrogen atom.

Crystal data of 22

Single crystal of **22** suitable for single-crystal structure analysis was obtained by recrystallization from MeCN. Black plate. $C_{42}H_{48}N_6O_6S_2$, M = 797.00, P1 bar (#2), a = 10.2153(8) Å, b = 14.5679(11) Å, c = 16.0551(12) Å, a = 107.972(8)°, b = 104.609(7)°, g = 106.675(8)°, V = 2019.1(3) Å^3, Z = 2, D_c = 1.311 g cm^{-3}. Independent reflection 7246 (all), T = 173 K, m = 16.46 cm^{-1}, R = 6.57%. CCDC 2063387.†

Computational methods

DFT calculations were performed with the Gaussian 09 [67] or Gaussian 16 [68] program packages. The geometries of the molecules were optimized using the B3LYP/6-31G* basis set. Terminal long alkyl groups were replaced by methyl groups in **13**, **15**, **19** and **21**. Stationary points were assessed by a vibration frequency analysis. TD-DFT calculations were performed for the optimized structure with the B3LYP/cc-pvdz basis set.

Preparation of 1

A mixture of 1,8-dichloroanthraquinone (847 mg, 3.06 mmol), toluidine (974 mg, 9.09 mmol) and $CsCO_3$ (3.90 g, 20.2 mmol) in dry toluene (45 mL) was degassed by bubbling with N_2. $Pd_2(dba)_3$ (109 mg, 119 μmol) and (±)-BINAP (327 mg, 525 μmol) were added at rt. The mixture was stirred at 110 °C for 38 h. The reaction was cooled to rt, and the solvent was removed under reduced pressure. The obtained product was dissolved in CH_2Cl_2 and H_2O. The aqueous layer was separated and extracted with CH_2Cl_2. The combined organic layer was dried over $MgSO_4$. After evaporation of the solvent under reduced pressure, the obtained crude product was purified by silica gel column chromatography (toluene) to give **1** (1.26 g, 98%) as a dark purple solid. The spectroscopic data were identical to the reported values.[58]

Preparation of 2 and 5

A mixture of 1,8-dichloroanthraquinone (850 mg, 3.07 mmol), *N*,*N*-dimethyl-1,4-phenylenediamine (1.15 mL, 9.20 mmol) and

$CsCO_3$ (4.14 g, 21.5 mmol) in dry toluene (40 mL) was degassed by bubbling with N_2. $Pd_2(dba)_3$ (140 mg, 153 μmol) and (±)-BINAP (382 mg, 613 μmol) were added at rt. The mixture was stirred at 110 °C for 36 h. The reaction was cooled to rt, and the mixture was diluted with $CHCl_3$ and H_2O. The aqueous layer was separated and extracted with $CHCl_3$. The combined organic layer was washed with brine and dried over $MgSO_4$. After evaporation of the solvent under reduced pressure, the obtained crude product was purified by silica gel column chromatography ($CHCl_3$), followed by GPC to give **2** (908 mg, 62%) and **5** (242 mg, 21%) as a dark blue solid and a dark purple solid, respectively.

Data for 2. Mp 276–277 °C; ^{1}H NMR (400 MHz): δ 11.1 (s, 2H), 7.61 (dd, J = 7.3, 1.2 Hz, 2H), 7.36 (dd, J = 8.5, 7.3 Hz, 2H), 7.26 (dd, J = 8.5, 1.2 Hz, 2H), 7.17 (d, J = 8.8 Hz, 4H), 6.77 (d, J = 8.8 Hz, 4H), 2.97 (s, 12H). ^{13}C NMR (100 MHz): δ 188.7, 184.3, 150.6, 148.6, 134.3, 133.7, 128.7, 126.7, 120.0, 116.3, 114.6, 113.3, 40.8. IR: 1656, 1612, 1561, 1522, 1494, 1477, 1440, 1392, 1373, 1350, 1294, 1236, 1216, 1182, 1166, 1126, 1089, 1066, 945, 866, 839, 817, 804, 750, 606 cm^{-1}. HRMS (EI) calcd for $C_{30}H_{28}O_2N_4$ 476.2212 (M^+); found: 476.2213. Anal. calcd for $C_{30}H_{28}O_2N_4 \cdot 0.33\ H_2O$: C, 74.67; H, 5.99; N, 11.61; found: C, 74.69; H, 5.86; N 11.44.

Data for 5. Mp 203–204 °C; ^{1}H NMR ($CDCl_3$): δ 11.03 (s, 1H), 8.28 (dd, J = 7.7, 1.4 Hz, 1H), 7.79 (dd, J = 8.0, 1.4 Hz, 1H), 7.61 (t, J = 7.8 Hz, 1H), 7.59 (dd, J = 7.3, 1.2 Hz, 1H), 7.40–7.38 (m, 1H), 7.30 (dd, J = 8.7, 1.2 Hz, 1H), 7.16 (d, J = 8.8 Hz, 2H), 6.77 (d, J = 8.8 Hz, 2H), 2.99 (s, 6H).^{13}C NMR ($CDCl_3$): δ 184.1, 182.9, 151.0, 148.8, 138.0, 135.6, 134.54, 134,51, 133.5, 132.7, 130.8, 128.0, 126.7, 126.5, 120.7, 116.4, 114.1, 113.2, 40.7. IR: 1665, 1630, 1615, 1594, 1577, 1526, 1357, 1310, 1243, 1184, 1131, 1064, 838, 788, 741 cm^{-1}. HRMS (EI) calcd for $C_{22}H_{17}O_2N_2Cl$ 376.0979 (M^+); found: 376.0977. Anal. calcd for $C_{22}H_{17}O_2N_2Cl$: C, 70.12; H, 4.55; N, 7.43; found: C, 70.20; H, 4.55; N 7.16.

Preparation of 3 [52]

A mixture of 1,8-dichloroanthraquinone (5.01 g, 18.1 mmol), *p*-toluenesulfonamide (9.20 g, 53.7 mmol), copper(II) acetate monohydrate (250 mg, 1.25 mmol) and potassium acetate (4.00 g, 40.8 mmol) in nitrobenzene (50 mL) was stirred at 200 °C under air for 14.5 h. After cooling to rt, the resulting mixture was diluted with water and $CHCl_3$. The aqueous layer was separated and extracted with $CHCl_3$. The combined organic layers were washed with brine and dried over $MgSO_4$. After evaporation of the solvent under reduced pressure, the obtained crude product was recrystallized from benzene to give compound **3** (6.16 g, 62%) as a yellow solid.

Mp: 274–275 °C. ^{1}H NMR (400 MHz): δ 11.8 (s, 2H), 8.02 (dd, J = 8.5, 1.2 Hz, 2H), 7.92 (dd, J = 7.5, 1.2 Hz, 2H), 7.86 (d, J = 8.5 Hz, 4H), 7.65 (br t, J = 8.1 Hz, 2H), 7.30 (d, J = 8.1 Hz, 4H), 2.38 (s, 6H). ^{13}C NMR (100 MHz): δ 190.6, 181.5, 144.6, 141.5, 136.2, 135.9, 133.6, 130.0, 127.3, 123.9, 122.3, 118.0, 21.6 IR: 3129, 1668, 1619, 1596, 1575, 1483, 1459, 1386, 1343, 1299, 1263, 1236, 1160, 1090, 993, 886, 863, 844, 812, 743, 718, 664, 563, 544, 513, 464 cm^{-1}. HRMS (FAB) calcd for $C_{28}H_{23}N_2O_6S_2$: 547.0998 [(M + H)$^+$]; found: 547.0992. Anal. calcd for $C_{28}H_{22}N_2O_6S_2$: C, 61.52 H, 4.06; N, 5.12. Found: C, 61.49 H, 4.21; N, 5.07.

Preparation of 4

A mixture of 1,8-dichloroanthraquinone (1.11 g, 4.00 mmol), 4-(dimethylamino)benzenesulfonamide (2.00 g, 9.99 mmol),[65] copper(II) acetate monohydrate (96.1 mg, 481 μmol) and potassium acetate (995 mg, 10.1 mmol) in nitrobenzene (40 mL) was stirred at 200 °C under air for 16 h. After cooling to rt, the resulting mixture was diluted with water and $CHCl_3$. The aqueous layer was separated and extracted with $CHCl_3$. The combined organic layers were washed with brine and dried over $MgSO_4$. After evaporation of the solvent under reduced pressure, the obtained crude product was suspended in toluene/EtOH (1/1, ~100 mL) and the insoluble material was collected by filtration. The obtained solid was repeatedly recrystallized from toluene/EtOH to give compound **4** (1.03 g, 43%) as a dark orange solid.

Mp: 278–280 °C. ^{1}H NMR (400 MHz): δ 11.72 (s, 2H), 8.03 (dd, J = 8.5, 1.2 Hz, 2H), 7.88 (dd, J = 7.6, 1.2 Hz, 2H), 7.78 (d, J = 9.2 Hz, 4H), 7.63 (t, J = 8.0 Hz, 2H), 6.62 (d, J = 9.2 Hz, 4H), 3.01 (s, 12H). ^{13}C NMR (100 MHz): δ 190.4, 181.9, 153.2, 141.9, 135.6, 133.6, 129.2, 123.9, 123.8, 121.8, 117.9, 110.9, 40.0. IR: 3112, 2904, 2822, 1672, 1618, 1599, 1552, 1522, 1476, 1455, 1380, 1344, 1298, 1264, 1222, 1148, 1089, 989, 944, 873, 852, 815, 70, 749, 715, 701, 674, 661, 643, 557, 544, 516, 460 cm^{-1}. HRMS (FAB) calcd for $C_{30}H_{28}N_4O_6S_2Na$: 627.1348 [(M + Na)$^+$]; found: 627.1350. Anal. calcd for $C_{30}H_{28}N_4O_6S_2 \cdot 0.5$(toluene): C, 61.83 H, 4.96; N, 8.61. Found: C, 61.90 H, 4.95; N8.60.

Preparation of 6 [55]

To a suspension of NaH (60% in oil, 333 mg, 8.33 mmol) in dry DMF (20 mL) was added **3** (303 mg, 554 μmol) under N_2. The mixture was stirred at rt for 45 min. To the resulting solution was added MeI (700 μL, 11.0 mmol) at this temperature. The mixture was stirred at rt for 12 h. The mixture was diluted with an excess amount of water. The resulting precipitate was collected by filtration, washed with water, and then dried under vacuum. Recrystallization from EtOH gave **6** (171 mg, 54%) as an orange crystalline solid.

Mp: 236–237 °C. ^{1}H NMR (400 MHz): δ 8.24 (dd, J = 7.8, 1.3 Hz, 2H), 7.70 (d, J = 7.8 Hz, 4H), 7.63 (t, J = 7.6 Hz, 2H), 7.47 (dd, J = 7.8, 1.3 Hz, 2H), 7.31 (d, J = 7.8 Hz, 4H), 3.24 (s, 6H), 2.43 (s, 6H). ^{13}C NMR (100 MHz): δ 182.6, 182.3, 143.5, 140.3, 136.0, 134.6, 133.6, 133.0, 129.6, 127.9, 126.9, 38.8, 21.6. IR: 3072, 2948, 2919, 1680, 1585, 1495, 1461, 1436, 1400, 1345, 1318, 1249, 1216, 1188, 1150, 1089, 1020, 1011, 957, 871, 850, 802, 752, 730, 688, 675, 651, 581, 563, 545, 517 cm^{-1}. HRMS (FAB) calcd for $C_{30}H_{27}N_2O_6S_2$: 575.1311 [(M + H)$^+$]; found: 575.1309. Anal. calcd for $C_{30}H_{26}N_2O_6S_2$: C, 62.70 H, 4.56; N, 4.87. Found: C, 62.55 H, 4.73; N, 4.78.

Preparation of 8 and 11

A mixture of 1,4-dichloroanthraquinone (854 mg, 3.08 mmol), *N*,*N*-dimethyl-1,4-phenylenediamine (1.25 mL, 10.0 mmol) and $CsCO_3$ (4.34 g, 22.5 mmol) in dry toluene (40 mL) was degassed

by bubbling with N_2. $Pd_2(dba)_3$ (140 mg, 153 μmol) and (±)-BINAP (402 mg, 646 μmol) were added at rt. The mixture was stirred at 110 °C for 47 h. The reaction was cooled to rt, and the mixture was diluted with $CHCl_3$ and H_2O. The aqueous layer was separated and extracted with $CHCl_3$. The combined organic layer was washed with brine and dried over $MgSO_4$. After evaporation of the solvent under reduced pressure, the obtained crude product was purified by silica gel column chromatography ($CHCl_3$), followed by recrystallization (EtOH for **8**, EtOH/$CHCl_3$ for **11**) to give **8** (234 mg, 16%) and **11** (742 mg, 64%) as a dark green solid and a dark purple solid, respectively.

Data for 8. Mp 262–264 °C; ^{1}H NMR (400 MHz): δ 12.34 (s, 2H), 8.41 (dd, J = 5.9, 3.4 Hz, 2H), 7.74 (dd, J = 5.9, 3.4 Hz, 2H), 7.31 (s, 2H), 7.14 (d, J = 8.8 Hz, 4H), 6.75 (d, J = 8.8 Hz, 4H), 2.97 (s, 12H). ^{13}C NMR (100 MHz): δ 182.3, 148.5, 145.5, 134.5, 132.2, 128.3, 126.3, 126.1, 125.2, 113.2, 110.0, 40.8. IR: 1611, 1589, 1567, 1547, 1521, 1501, 1458, 1440, 1401, 1364, 1339, 1258, 1216, 1187, 1162, 1132, 1069, 1027, 1007, 967, 944, 922, 881, 850, 823, 800, 755, 727, 673, 640, 607, 562, 517, 466, 432 cm^{-1}. HRMS (EI) calcd for $C_{30}H_{28}O_2N_4$ 476.2212 (M^+); found: 476.2211. Anal. Calcd for $C_{30}H_{28}O_2N_4 \cdot 2H_2O$: C, 70.29; H, 6.29; N, 10.93; found: C, 70.32; H, 6.12; N 10.93.

Data for 11. Mp 195–197 °C; ^{1}H NMR (400 MHz): δ 11.51 (s, 1H), 8.29–8.23 (m, 2H), 7.80–7.71 (m, 2H), 7.37 (dd, J = 9.5, 0.5 Hz, 1H), 7.19 (d, J = 9.5 Hz, 1H), 7.14 (d, J = 8.8 Hz, 2H), 6.77 (d, J = 8.8 Hz, 1H), 2.99 (s, 6H). ^{13}C NMR (125 MHz): δ 184.4, 183.0, 150.6, 149.0, 138.7, 133.9, 133.8, 133.7, 133.3, 129.9, 127.4, 126.9, 126.8, 126.3, 123.0, 120.8, 114.1, 113.2, 40.7. IR: 1668, 1625, 1610, 1586, 1576, 1521, 1491, 1480, 1444, 1355, 1293, 1257, 1240, 1181, 1125, 807, 734, 722 cm^{-1}. HRMS (EI) calcd for $C_{22}H_{17}O_2N_2Cl$ 376.0979 (M^+); found: 376.0977. Anal. Calcd for $C_{22}H_{17}O_2N_2Cl$: C, 70.12; H, 4.55; N, 7.43; found: C, 70.16; H, 4.51; N 7.30.

Preparation of 9 [52]

A mixture of 1,4-dichloroanthraquinone (5.00 g, 18.1 mmol), *p*-toluenesulfonamide (9.20 g, 53.7 mmol), copper(II) acetate monohydrate (250 mg, 1.25 mmol), and potassium acetate (4.00 g, 40.8 mmol) in nitrobenzene (50 mL) was stirred at 200 °C under air for 10 h. After cooling to rt, the resulting mixture was diluted with water and $CHCl_3$. The aqueous layer was separated and extracted with $CHCl_3$. The combined organic layers were washed with brine and dried over $MgSO_4$. The obtained crude solid was washed with a small amount of $CHCl_3$ and then recrystallized from $CHCl_3$ to give compound **9** (2.04 g) as a red solid. Combined filtrate was subjected to silica gel column chromatography ($CHCl_3$) to give an additional amount of compound **9** (5.18 g). Total yield: 7.22 g (73%).

Mp: 245–246 °C. ^{1}H NMR (400 MHz): δ 12.3 (s, 2H), 8.22 (dd, J = 9.2, 5.9 Hz, 2H), 7.97 (s, 2H), 7.80 (dd, J = 9.2, 5.9 Hz, 2H), 7.76 (d, J = 8.2 Hz, 4H), 7.24 (d, J = 8.2 Hz, 4H), 2.36 (s, 6H). ^{13}C NMR (100 MHz): δ 186.2, 144.5, 137.4, 136.3, 134.8, 132.9, 129.9, 127.3, 127.2, 126.3, 117.1, 21.5. IR: 3019, 1639, 1590, 1475, 1379, 1352, 1287, 1254, 1186, 1164, 1090, 1072, 971, 920, 896, 859, 839, 818, 726, 714, 656, 579, 558, 544 cm^{-1}. HRMS (FAB) calcd for $C_{28}H_{22}N_2O_6S_2Na$: 569.0817 [(M + Na)$^+$]; found: 569.0817. Anal. calcd for $C_{28}H_{22}N_2O_6S_2$: C, 61.52 H, 4.06; N, 5.12. Found: C, 61.60 H, 4.31; N,5.05.

Preparation of 10

Route A. A mixture of 1,4-diaminoanthraquinone (776 mg, 3.26 mmol) and 4-(dimethylamino)benzenesulfonyl chloride (1.50 g, 6.84 mmol)[65] in dry pyridine (40 mL) was stirred at rt for 24 h and then at 70 °C for 15 h. After cooling to rt, the solvent was removed under reduced pressure. The resulting mixture was dissolved in $CHCl_3$ and the solution was washed with brine and dried over $MgSO_4$. After evaporation of the solvent under reduced pressure, the obtained crude product was recrystallized from toluene/EtOH to give **10** (803 mg, 41%) as a red solid.

Mp: 287–288 °C. ^{1}H NMR (400 MHz): δ 12.25 (s, 2H), 8.24 (dd, J = 5.9, 3.3 Hz, 2H), 7.95 (s, 2H), 7.79 (dd, J = 5.9, 3.3 Hz, 2H), 7.69 (d, J = 9.1 Hz, 4H), 6.58 (d, J = 9.1 Hz, 4H), 2.99 (s, 12H). ^{13}C NMR (125 MHz): δ 186.2, 153.1, 137.7, 134.5, 133.1, 129.2, 127.2, 126.2, 123.9, 116.6, 110.9, 40.0. IR: 3448, 3098, 2896, 1639, 1597, 1552, 1521, 1473, 1449, 1375, 1349, 1326, 1286, 1253, 1206, 1153, 1091, 1069, 998, 970, 919, 892, 836, 824, 816, 794, 773, 728, 708, 642, 558, 544 cm^{-1}. HRMS (FAB) calcd for $C_{30}H_{28}N_4O_6S_2$-Na: 627.1348 [(M + Na)$^+$]; found: 627.1347. Anal. calcd for $C_{30}H_{28}N_4O_6S_2 \cdot 0.33$ toluene: C, 61.12 H, 4.86; N, 8.82. Found: C, 61.22 H, 5.06; N, 8.86.

Route B. A mixture of 1,4-dichloroanthraquinone (570 mg, 2.06 mmol), 4-(dimethylamino)benzenesulfonamide (1.00 g, 4.50 mmol), copper(II) acetate monohydrate (73.3 mg, 367 μmol) and potassium acetate (540 mg, 5.50 mmol) in nitrobenzene (40 mL) was stirred at 200 °C under air for 15 h. After cooling to rt, the resulting mixture was diluted with water and $CHCl_3$. The aqueous layer was separated and extracted with $CHCl_3$. The combined organic layers were washed with brine and dried over $MgSO_4$. After evaporation of the solvent under reduced pressure, the obtained crude product was recrystallized from toluene/EtOH to give compound **10** (292 mg, 23%) as a red solid. The spectroscopic data were identical to those for the product synthesized through route A.

Preparation of 12 [55]

A mixture of **9** (200 mg, 366 μmol), K_2CO_3 (506 mg, 3.66 mmol) and MeI (455 μL, 7.32 mmol) in DMF (10 mL) was stirred at 50 °C for 13.5 h in a sealed glass pressure vessel. After cooling to rt, the mixture was diluted with H_2O. The resulting precipitate was collected by filtration, washed with H_2O, and then dried under vacuum. Recrystallization from $CHCl_3$/EtOH gave **12** (195 mg, 93%) as a yellow solid.

Mp: 228–229 °C (decomp.). ^{1}H NMR (400 MHz, 50 °C): δ 7.92 (br s, 2H), 7.68 (dd, J = 5.7, 3.2 Hz, 2H), 7.57 (t, J = 8.2 Hz, 4H), 7.42 (s, 2H), 7.23 (d, J = 8.2 Hz, 4H), 3.35 (s, 6H), 2.39 (s, 6H). ^{13}C NMR (125 MHz, 50 °C): δ 182.5, 143.5, 140.3, 136.5, 136.4, 134.2, 134.1, 133.6, 129.6, 127.7, 126.6, 38.8, 21.5. IR: 1670, 1590, 1463, 1348, 1322, 1305, 1254, 1201, 1156, 1087, 931, 910, 877, 809, 795, 727, 713, 679, 636, 596, 549, 516 cm^{-1}. HRMS (FAB) calcd for $C_{30}H_{27}N_2O_6S_2$: 575.1311 [(M + H)$^+$]; found: 575.1310. Anal. calcd for $C_{30}H_{26}N_2O_6S_2$: C, 62.70 H, 4.56; N, 4.87. Found: C, 62.88 H, 4.57; N, 4.82.

Preparation of 13

A mixture of 1,5-dichloroanthraquinone (845 mg, 3.05 mmol), 4-*tert*-butylaniline (1.45 mL, 9.13 mmol) and $CsCO_3$ (3.91 g, 20.3 mmol) in dry toluene (40 mL) was degassed by bubbling with N_2. $Pd_2(dba)_3$ (117 mg, 127 μmol) and (±)-BINAP (333 mg, 535 μmol) were added at rt. The mixture was stirred at 110 °C for 38 h. The reaction was cooled to rt, and the resulting solid was collected by filtration and washed with toluene to give **13** (1.29 g, 84%) as a dark purple crystalline solid. The spectroscopic data were identical to the reported values.[58]

Preparation of 14 [52]

A mixture of 1,5-dichloroanthraquinone (4.71 g, 17.0 mmol), 4-*tert*-butylbenzenesulfonamide (10.0 g, 46.9 mmol), copper(II) acetate monohydrate (218 mg, 1.09 mmol), and potassium acetate (3.49 g, 35.6 mmol) in nitrobenzene (50 mL) was stirred at 200 °C under air for 11.5 h. After cooling to rt, the resulting mixture was diluted with water and $CHCl_3$. The aqueous layer was separated and extracted with $CHCl_3$. The combined organic layers were washed with brine and dried over $MgSO_4$. After evaporation of the solvent under reduced pressure, the obtained solid was subjected to silica gel column chromatography ($CHCl_3$) followed by recrystallization from toluene to give compound **14** as a yellow solid (6.82 g, 63%).

Mp: >300 °C. ^{1}H NMR (400 MHz): δ 12.1 (s, 2H), 7.99 (dd, J = 8.5, 1.1 Hz, 2H), 7.96 (dd, J = 7.7, 1.1 Hz, 2H), 7.87–7.83 (m, 4H), 7.68 (t, J = 8.2 Hz), 7.49–7.44 (m, 4H), 1.26 (s, 18H). ^{13}C NMR (100 MHz): δ 185.8, 157.4, 141.3, 136.2, 135.8, 134.5, 127.1, 126.3, 123.4, 122.5, 116.9, 35.2, 30.9. IR: 3080, 2965, 1637, 1593, 1475, 1385, 1348, 1264, 1199, 1163, 1113, 1086, 1055, 889, 835, 770, 753, 711, 654, 624, 570, 548 cm^{-1}. HRMS (FAB) calcd for $C_{34}H_{35}N_2O_6S_2$: 631.1937 [(M + H)$^+$]; found: 631.1937. Anal. calcd for $C_{34}H_{34}N_2O_6S_2$: C, 64.74 H, 5.43; N, 4.44. Found: C, 64.90 H, 5.49; N, 4.37.

Preparation of 4-(dibutylamino)benzenesulfonyl chloride

A mixture of *N*,*N*-dibutylaniline (8.47 g, 41.2 mmol) and bis(-trimethylsilyl) sulfate (10.0 g, 41.2 mmol) was stirred at 170 °C under a nitrogen atmosphere for 4 h. After cooling to rt, the resulting solid was washed with ether and H_2O, and then dried under vacuum to give 4-(dibutylamino)benzenesulfonic acid, which was used for the next reaction directly without further purification. To the obtained 4-(dibutylamino)benzenesulfonic acid in dry CH_2Cl_2 (110 mL) was added PCl_5 (8.59 g, 41.2 mmol) at 0 °C. The mixture was warmed gradually to rt and stirred for 24 h under a nitrogen atmosphere. The solvent was removed under reduced pressure and the product was dissolved in ether. The solution was washed with H_2O and dried over $MgSO_4$. After evaporation of the solvent under reduced pressure, the crude product was subjected to silica gel column chromatography (hexane/ether = 100/20) to give 4-(dibutylamino)benzenesulfonyl chloride (8.19 g, 65% in two steps) as a yellow oil.

^{1}H NMR (400 MHz): δ 7.79 (d, J = 9.4 Hz, 2H), 6.62 (d, J = 9.4 Hz, 2H), 3.36 (t, J = 7.8 Hz, 4H), 1.65–1.55 (m, 4H), 1.38 (sext, J = 7.5 Hz, 4H) 0.98 (t, J = 7.3 Hz, 6H). ^{13}C NMR (100 MHz): δ 152.6, 129.6, 128.4, 110.3, 50.9, 29.0, 20.2, 13.9. IR: 2959, 2933, 2873, 1591, 1516, 1467, 1409, 1368, 1314, 1292, 1165, 1086, 992, 926, 814, 655, 559, 542, 501 cm^{-1}. HRMS (EI) calcd for $C_{14}H_{22}ClNO_2S$: 303.1060 [(M + H)$^+$]; found: 303.1062.

Preparation of 15

A mixture of 1,5-diaminoanthraquinone (991 mg, 4.16 mmol) and 4-(dibutylamino)benzenesulfonyl chloride (2.65 g, 8.74 mmol) in dry pyridine (50 mL) was stirred at 70 °C for 45 h. After cooling to rt, the solvent was removed under reduced pressure. The resulting mixture was dissolved in $CHCl_3$ and the solution was washed with brine and dried over $MgSO_4$. After evaporation of the solvent under reduced pressure, the obtained crude product was recrystallized from toluene/EtOH to give **15** (2.12 g, 66%) as a red-brown solid.

Mp: 256–257 °C. ^{1}H NMR (400 MHz): δ 11.97 (s, 2H), 8.01 (dd, J = 8.5, 1.1 Hz, 2H), 7.93 (dd, J = 7.7, 1.1 Hz, 2H), 7.69 (d, J = 9.2 Hz, 4H), 7.66 (sext, J = 8.0 Hz, 2H), 6.52 (d, J = 9.2 Hz, 4H), 3.24 (t, J = 7.8 Hz, 8H), 1.55–1.46 (m, 8H), 1.31 (sext, J = 7.6 Hz, 8H), 0.92 (t, J = 7.3 Hz, 12H). ^{13}C NMR (100 MHz): δ 185.8, 151.4, 141.8, 135.6, 134.6, 129.3, 123.1, 121.8, 116.6, 110.4, 50.7, 29.0, 20.2, 13.9. IR: 3455, 3094, 2957, 2930, 2871, 1637, 1593, 1509, 1474, 1379, 1348, 1261, 1228, 1207, 1151, 1092, 1054, 995, 929, 917, 881, 825, 813, 774, 734, 715, 707, 654, 608, 566, 550, 514, 443, 418 cm^{-1}. HRMS (FAB) calcd for $C_{42}H_{52}N_4O_6S_2Na$: 795.3226 [(M + Na)$^+$]; found: 795.3228. Anal. calcd for $C_{42}H_{52}N_4O_6S_2$·toluene: C, 65.26 H, 6.78; N, 7.25. Found: C, 65.42 H, 6.82; N, 7.16.

Preparation of 16

A mixture of 1,5-dichloroanthraquinone (850 mg, 3.07 mmol), *N*,*N*-dimethyl-1,4-phenylenediamine (1.25 mL, 10.0 mmol) and $CsCO_3$ (4.14 g, 21.5 mmol) in dry toluene (40 mL) was degassed by bubbling with N_2. $Pd_2(dba)_3$ (176 mg, 192 μmol) and (±)-BINAP (470 mg, 755 μmol) were added at rt. The mixture was stirred at 110 °C for 42 h. The reaction was cooled to rt, and the resulting mixture was diluted with water and $CHCl_3$. The aqueous layer was separated and extracted with $CHCl_3$. The combined organic layers were washed with brine and dried over $MgSO_4$. After evaporation of the solvent under reduced pressure, the resulting purple solid was subjected to silica gel column chromatography ($CHCl_3$) to give **16** (694 mg, 61%) as a dark purple crystalline solid.

Mp: 213–214 °C. ^{1}H NMR (400 MHz): δ 11.04 (s, 1H), 8.34 (dd, J = 7.7, 1.4 Hz, 1H), 7.74 (dd, J = 8.0, 1.4 Hz, 1H), 7.66 (t, J = 7.9 Hz, 1H), 7.60 (dd, J = 7.3, 1.1 Hz, 1H), 7.44 (dd, J = 8.5, 7.5 Hz, 1H), 7.17 (d, J = 8.8 Hz, 2H), 6.78 (d, J = 8.8 Hz, 2H), 2.99 (s, 6H). ^{13}C NMR (100 MHz): δ 183.3, 182.5, 150.8, 148.9, 137.6, 136.5, 135.6, 135.2, 134.5, 133.4, 129.4, 127.8, 126.7, 126.3, 119.4, 117.2, 113.2, 112.5, 40.7. IR: 1665, 1627, 1591, 1577, 1566, 1522, 1500, 1308, 1258, 1224, 1193, 1158, 808, 760, 709 cm^{-1}. HRMS (EI) calcd for $C_{22}H_{17}N_2O_2Cl$: 376.0979 (M$^+$); found: 376.0976. Anal. calcd for $C_{22}H_{17}N_2O_2Cl$: C, 70.12 H, 4.55; N, 7.43. Found: C, 70.02 H, 4.58; N, 7.34.

Preparation of 17

A mixture of 1,5-dichloroanthraquinone (1.17 g, 4.22 mmol), 4-(dimethylamino)benzenesulfonamide (2.00 g, 10.0 mmol), copper(II) acetate monohydrate (125 mg, 626 μmol), and potassium acetate (900 mg, 9.15 mmol) in nitrobenzene (80 mL) was stirred at 200 °C under air for 21.5 h. After cooling to rt, the resulting mixture was diluted with water and $CHCl_3$. The aqueous layer was separated and extracted with $CHCl_3$. The combined organic layers were washed with brine and dried over $MgSO_4$. After evaporation of the solvent under reduced pressure, the obtained brown solid was recrystallized from toluene/EtOH to remove insoluble material. After evaporation of the solvent of the filtrate under reduced pressure, the obtained solid was suspended in $CHCl_3$ and filtered. The filtrate was subjected to silica gel column chromatography ($CHCl_3$) to give compound **17** as an orange solid (399 mg, 21%).

Mp: 245–247 °C. ^{1}H NMR (400 MHz): δ 11.85 (s, 1H), 8.30 (dd, J = 7.8, 1.4 Hz, 1H), 7.99 (dd, J = 8.5, 1.1 Hz, 1H), 7.91 (dd, J = 7.7, 1.1 Hz, 1H), 7.79 (dd, J = 8.0, 1.4 Hz, 1H), 7.76 (d, J = 9.2 Hz, 2H), 7.69 (t, J = 7.8 Hz, 1H), 7.66 (d, J = 8.1 Hz, 1H), 6.59 (d, J = 9.2 Hz, 2H), 2.99 (s, 6H). ^{13}C NMR (100 MHz): δ 185.4, 181.2, 153.1, 141.4, 137.8, 136.3, 135.8, 135.3, 134.9, 133.8, 129.2, 129.1, 127.0, 123.9, 122.7, 122.1, 116.6, 110.8, 40.0. IR: 3097, 1675, 1636, 1598, 1573, 1553, 1523, 1477, 1468, 1447, 1380, 1340, 1322, 1285, 1268, 1208, 1197, 1149, 1093, 1071, 1036, 997, 935, 909, 846, 839, 812, 759, 708, 644, 557, 544, 431 cm^{-1}. HRMS (FAB) calcd for $C_{22}H_{17}N_2O_4SClNa$: 463.0495 [(M + Na)$^+$]; found: 463.0491. Anal. calcd for $C_{22}H_{17}N_2O_4SCl$: C, 59.93 H, 3.89; N, 6.35. Found: C, 59.79 H, 3.82; N, 6.23.

Preparation of 18 [55]

To a suspension of NaH (60% in oil, 380 mg, 9.51 mmol) in dry DMF (30 mL) was added **14** (400 mg, 634 μmol) under N_2. The mixture was stirred at rt for 45 min. To the resulting solution was added MeI (790 μL, 12.7 mmol) at this temperature. The mixture was stirred at rt for 16.5 h. The mixture was diluted with an excess amount of water. The resulting precipitate was collected by filtration, washed with water, and then dried under vacuum. Recrystallization from $CHCl_3$/EtOH gave **18** (177 mg, 42%) as a yellow solid.

Mp: 268–270 °C (decomp.). ^{1}H NMR (400 MHz, 50 °C): δ 8.08 (br d, J = 7.8 Hz, 2H), 7.65(t, J = 7.8 Hz, 2H), 7.63 (d, J = 8.5 Hz, 4H), 7.50 (d, J = 7.8 Hz, 2H), 7.44 (d, J = 8.5 Hz, 4H), 3.35 (s, 6H), 1.33 (s, 18H). ^{13}C NMR (125 MHz, 50 °C): δ 181.8, 156.4, 140.0, 137.0, 136.8, 136.4, 133.9, 127.9, 127.5, 125.8, 36.7, 35.2, 31.1. IR: 3076, 2957, 1675, 1596, 1580, 1457, 1438, 1400, 1349, 1310, 1267, 1190, 1158, 1112, 1085, 1018, 877, 825, 807, 773, 756, 710, 626, 581, 552 cm^{-1}. HRMS (FAB) calcd for $C_{36}H_{39}N_2O_6S_2$: 659.2250 [(M + H)$^+$]; found: 659.2250. Anal. calcd for $C_{36}H_{38}N_2O_6S_2$: C, 65.60 H, 5.81; N, 4.25. Found: C, 62.60 H, 5.86; N, 4.22.

Preparation of 19

A mixture of 1,4,5,8-tetrachloroanthraquinone (1.04 g, 3.01 mmol), 4-*tert*-butylaniline (2.90 mL, 18.1 mmol) and $CsCO_3$ (7.80 g, 40.8 mmol) in dry toluene (50 mL) was degassed by bubbling with N_2. $Pd_2(dba)_3$ (110 mg, 120 μmol) and (±)-BINAP (330 mg, 530 μmol) were added at rt. The mixture was stirred at 110 °C for 49 h. The reaction was cooled to rt, and the resulting crystalline solid was collected by filtration, washed with toluene and H_2O, and dried under vacuum to give **19** (2.06 g, 86%) as a dark green crystalline solid. The spectroscopic data were identical to the reported values.[59]

Preparation of 20 [52]

A mixture of 1,4,5,8-tetrachloroanthraquinone (3.00 g, 8.67 mmol), 4-*tert*-butylbenzenesulfonamide (10.0 g, 46.9 mmol), copper(II) acetate monohydrate (277 mg, 1.39 mmol), and potassium acetate (3.57 g, 36.4 mmol) in nitrobenzene (50 mL) was stirred at 200 °C under air for 18.5 h. After cooling to rt, the resulting mixture was diluted with water and $CHCl_3$. The aqueous layer was separated and extracted with $CHCl_3$. The combined organic layers were washed with brine and dried over $MgSO_4$. The obtained crude solid was subjected to silica gel column chromatography ($CHCl_3$) followed by recrystallization from toluene to give compound **20** as a dark purple solid (5.11 g, 56%).

Mp: decomposed above 270 °C. ^{1}H NMR (400 MHz): δ 11.8 (s, 4H), 7.97 (s, 4H), 7.75 (d, J = 8.7 Hz, 8H), 7.50 (d, J = 8.7 Hz, 8H), 1.28 (s, 36H). ^{13}C NMR (100 MHz): δ 188.6, 157.8, 137.4, 136.0, 127.1, 126.6, 126.5, 116.9, 35.3, 30.9. IR: 2964, 1595, 1479, 1377, 1221, 1198, 1167, 1112, 1084, 981, 862, 837, 791, 755, 647, 622, 571, 546 cm^{-1}. HRMS (FAB) calcd for $C_{54}H_{60}N_4O_{10}S_4Na$: 1075.3090 [(M + Na)$^+$]; found: 1075.3085. Anal. calcd for $C_{54}H_{60}N_4O_{10}S_4$: C, 61.57 H, 5.74; N, 5.32. Found: C, 61.81 H, 5.88; N, 5.24.

Preparation of 4-(dihexylamino)benzenesulfonyl chloride

A mixture of *N*,*N*-dihexylaniline (10.8 g, 41.3 mmol) and bis(-trimethylsilyl) sulfate (10.0 g, 41.2 mmol) was stirred at 170 °C under a nitrogen atmosphere for 3 h. After cooling to rt, the resulting solid was washed with ether and the dried under vacuum to give 4-(dihexylamino)benzenesulfonic acid, which was used for the next reaction directly without further purification. To the obtained 4-(dihexylamino)benzenesulfonic acid in dry CH_2Cl_2 (110 mL) was added PCl_5 (8.73 g, 41.9 mmol) at 0 °C. The mixture was warmed gradually to rt and stirred for 41 h under a nitrogen atmosphere. The solvent was removed under reduced pressure and the product was dissolved in ether. The solution was washed with H_2O and dried over $MgSO_4$. After evaporation of the solvent under reduced pressure, the crude product was subjected to silica gel column chromatography (hexane/ether = 100/20) to give 4-(dihexylamino)benzenesulfonyl chloride (9.40 g, 63% in two steps) as a yellow oil.

^{1}H NMR (400 MHz): δ 7.79 (d, J = 9.3 Hz, 2H), 6.61 (d, J = 9.3 Hz, 2H), 3.34 (t, J = 7.8 Hz, 4H), 1.67–1.57 (m, 4H), 1.38–1.29 (m, 4H), 0.91 (t, J = 6.8 Hz, 6H). ^{13}C NMR (125 MHz): δ 152.6, 129.6, 128.6, 110.4, 51.2, 31.6, 26.9, 26.7, 22.6, 14.0. IR: 2957, 2931, 2859, 1591, 1516, 1469, 1409, 1369, 1164, 1087, 814, 656, 561 cm^{-1}. HRMS (EI) calcd for $C_{18}H_{30}NO_2SCl$: 359.1686 (M$^+$); found: 359.1685.

Preparation of 21

To a solution of 1,4,5,8-tetraaminoanthraquinone (Disperse Blue 1, Aldrich, 1.45 g, 5.39 mmol) in dry pyridine (100 mL) was added 4-(dihexylamino)benzenesulfonyl chloride (9.40 g, 24.2 mmol). The mixture was stirred at rt for 77 h under a nitrogen atmosphere. After removal of the solvent under reduced pressure, the resulting crude product was purified by silica gel column chromatography (PhH/AcOEt = 100/0 → 100/4), and recrystallized from toluene/EtOH to give **21** (1.47 g, 18%) as a dark purple solid.

Mp: 116–118 °C. ^{1}H NMR (400 MHz): δ 11.87 (s, 4H), 7.95 (s, 4H), 7.67 (d, J = 9.1 Hz, 4H), 6.54 (d, J = 9.1 Hz, 4H), 1,60–1.46 (m, 16H), 1.37–1.25 (m, 16H) 0.89 (t, J = 6.7 Hz, 24 H). ^{13}C NMR (125 MHz): δ 188.6, 151.5, 137.5, 129.3, 126.1, 122.6, 116.4, 110.6, 51.0, 31.6, 26.9, 26.6, 22.6, 14.0. IR: 3119, 2954, 2929, 2857, 1594, 1554, 1514, 1479, 1405, 1367, 1255, 1217, 1156, 1092, 997, 978, 858, 816, 789, 659, 558 cm^{-1}. HRMS (FAB) calcd for $C_{86}H_{128}N_8O_{10}S_4Na$: 1583.8534 [(M + Na)$^+$]; found: 1583.8536. Anal. Calcd for $C_{86}H_{128}N_8O_{10}S_4$·toluene: C, 66.12 H, 8.26; N, 7.17. Found: C, 66.12 H, 8.40; N, 7.09.

Preparation of 22

A mixture of **20** (4.50 g, 4.27 mmol) and conc. H_2SO_4 (100 mL) was stirred at 100 °C. After cooling to rt, the mixture was poured into ice water (*ca.* 600 mL). The mixture was basified with NaOH and the resulting precipitate was collected by filtration, washed with H_2O and dried under vacuum to give a blue solid (5.36 g), which was used for the next reaction without further purification. A mixture of the product, 4-(dihexylamino)benzenesulfonyl chloride (5.50 g, 18.1 mmol) in pyridine was stirred at 70 °C for 40 h. After cooling to rt, the solvent was removed under reduced pressure. The product was dissolved in $CHCl_3$. The solution was washed with brine and dried over $MgSO_4$. After evaporation of the solvent under reduced pressure, the resulting blue solid was purified by silica gel column chromatography (PhH/AcOEt = 9/1), followed by recrystallization from toluene/EtOH to give pure **22** (494 mg, 14% in two steps) as a dark purple solid.

Mp: 230–231 °C. ^{1}H NMR (400 MHz): δ 13.11 (s, 2H), 7.695 (s, 2H), 7.695 (d, J = 9.2 Hz, 4H), 7.20–6.85 (br s, 4H), 6.63 (s, 2H), 6.55 (d, J = 9.1 Hz, 4H), 3.25 (t, J = 7.6 Hz, 8H), 1.59–1.47 (m, 8H), 1.33 (hext, J = 7.4 Hz, 8H), 0.93 (t, J = 7.4 Hz, 12H). ^{13}C NMR (125 MHz): δ 185.0, 151.2, 146.1, 136.3, 129.2, 128.4, 123.8, 123.1, 119.0, 110.5, 108.8, 50.7, 29.1, 20.2, 13.9. IR: 3440, 3290, 2957, 2931, 2870, 1650, 1601, 1571, 1539, 1515, 1472, 1451, 1408, 1381, 1349, 1318, 1298, 1251, 1204, 1179, 1146, 1092, 995, 983, 926, 900, 873, 847, 821, 776, 720, 656, 561, 516, 507, 490, 441 cm^{-1}. HRMS (FAB) calcd for $C_{42}H_{54}N_6O_6S_2Na$: 825.3444 [(M + Na)$^+$]; found: 825.3450. Anal. calcd for $C_{42}H_{54}N_6O_6S_2$: C, 62.82 H, 6.78; N, 10.47. Found: C, 62.83 H, 6.50; N, 10.43.

Preparation of 23 [55]

To a suspension of NaH (60% in oil, 304 mg, 7.60 mmol) in dry DMF (30 mL) was added **20** (400 mg, 380 μmol) under N_2. The mixture was stirred at rt for 45 min. To the resulting solution was added MeI (710 μL, 11.4 mmol) at this temperature. The mixture was stirred at rt for 17 h. The mixture was diluted with an excess amount of water. The resulting precipitate was collected by filtration, washed with water, and then dried under vacuum. Recrystallization from $CHCl_3$/EtOH gave **23** (264 mg, 63%) as a yellow solid.

Mp: 253–255 °C (decomp.). ^{1}H NMR (400 MHz): δ 7.76 (d, J = 8.6 Hz, 8H), 7.56 (d, J = 8.6 Hz, 8H), 7.25 (s, 4H), 3.20 (s, 12H), 1.37 (s, 36H). ^{13}C NMR (125 MHz): δ 181.8, 156.8, 139.2, 136.0, 135.0, 134.5, 127.9, 126.0, 39.2, 35.2, 31.2. IR: 2964, 2871, 1702, 1595, 1477, 1397, 1349, 1333, 1307, 1269, 1217, 1160, 1111, 1085, 1042, 936, 888, 865, 842, 812, 793, 762, 671, 630, 601, 580, 547 cm^{-1}. HRMS (FAB) calcd for $C_{58}H_{69}N_4O_{10}S_4$: 1109.3897 [(M + H)$^+$]; found: 1109.3899. Anal. calcd for $C_{58}H_{68}N_4O_{10}S_4$: C, 62.79 H, 6.18; N, 5.05. Found: C, 62.57 H, 6.13; N, 5.00.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

This work was partly supported by JSPS KAKENHI Grant numbers JP17K05769, JP20H04655 and JP20K05442, the Murata Science Foundation, 2020 Mitsui Chemical Award in Synthetic Organic Chemistry, Japan, Tobe Maki Scholarship Foundation, Iketani Science and Technology Foundation, Yamaguchi Educational and Scholarship Foundation, and the research program "Dynamic Alliance for Open Innovation Bridging Human, Environment and Materials" from MEXT, Japan.

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