Characterisation of 'sandwich' charge-transfer complexes composed of bis-anthracene donors and aromatic acceptors

Seung-Hwan Lee,[a] Koichiro Imamura,[b] Joe Otsuki,*[,a] Koji Araki[a] and Manabu Seno[b]

[a] *Institute of Industrial Science, University of Tokyo, 7-22-1 Roppongi, Minato-ku, Tokyo 106, Japan*

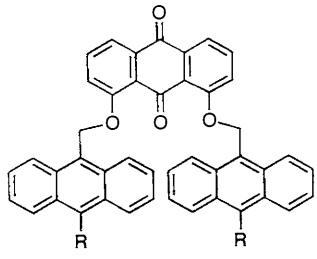
[b] *College of Science & Technology, Nihon University, 1-8-14 Kandasurugadai, Chiyoda-ku, Tokyo 101, Japan*

Properties of 'sandwich' charge-transfer (CT) complexes composed of bis-anthracene host compounds, in which two anthracences are connected by an anthraquinone spacer, and various aromatic acceptors have been systematically studied. Complexation stronger than that seen in monomer model compounds was observed in all cases. Thermodynamic analysis revealed that this enhanced binding to acceptors is due to larger enthalpic gain accompanied by a lower entropy loss effected by preorganization of the host. The major factor that determines the association constants is not the strength but the steric features of acceptor. Binding constants for fluorenones with nitro residues in the bay region are smaller because of the bulkiness of the substituents. It has been established that the CT complexes are of the weak b_π–a_π type from the analysis of the CT absorption energy. Complexation-induced chemical shifts in the ^{1}H NMR spectra indicate highly oriented guest inclusion and have revealed some geometrical features of the complexes.

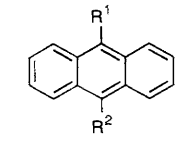
Since the classical experimental work by Benesi and Hildebrand[1] on the absorption spectra of mixtures of electron donors and acceptors, and the theoretical description of the results in terms of charge transfer (CT) by Mulliken,[2] there has been continued unabated interest in the CT complex, and a wide variety of donor-acceptor systems have been investigated.[3,4] Until recently, in the case of π-donor–π-acceptor systems, almost all studies have been concerned with simple 1:1 complexes, which usually associate very weakly in solution. Recent interest in molecular recognition and supramolecular assembly[5,6] has yielded a new family of CT species,[7,8] *viz.*, inclusion or sandwich-type CT complexes, in which an acceptor is included in a cavity or cleft made by donors, and *vice-versa*, and the association constants are relatively large.

We have reported that a bis-anthracene host molecule, 1,8-bis[(9-anthryl)methoxy]-9,10-anthraquinone (**1a**) binds aromatic acceptors with larger association constants than mono-anthracene models.[9] The two anthryl residues project in the same direction from the anthraquinone spacer and lie face to face. There is an effective cleft between the anthryl donors for accommodating an aromatic acceptor. For instance, 2,4,7-trinitrofluorenone (TNF) and **1a** form a one-to-one complex with an association constant (K_a) of the order of 10^2 M^{-1} in chloroform. It has been established that the acceptor is sandwiched between the two anthryl arms in solution, based on the complexation-induced chemical shifts (CIS) seen in the ^{1}H NMR spectrum and the quantitative calculation of the ring current effect. Recently, the X-ray crystal structure of the complex with TCNQ has been determined which indeed proved the sandwich motif of complexation in the solid state as well.[10]

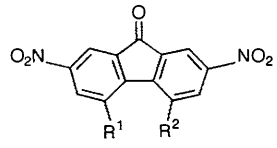
We report here systematic characterisation of the sandwich CT complex composed of **1a** and more soluble derivatives with alkyl substituents† (**1b** and **1c**) with aromatic acceptors by means of thermodynamic studies, visible absorption and ^{1}H NMR spectroscopy. The results for the bis-donor systems are compared with those for the usual mono-donors (anthracene derivatives) and the 'bis' effect will be demonstrated.



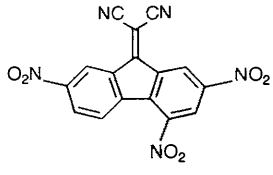
1a R = H
1b R = C_4H_9
1c R = $C_{12}H_{25}$



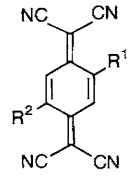
A R^1 = H, R^2 = H
MA R^1 = CH_3, R^2 = H
DMA R^1 = CH_3, R^2 = CH_3



DNF R^1 = H, R^2 = H
TNF R^1 = NO_2, R^2 = H
TENF R^1 = NO_2, R^2 = NO_2



TNFMN



TCNQ R^1 = H, R^2 = H
DMTCNQ R^1 = CH_3, R^2 = CH_3

† For instance, solubilities of **1a**, **1b** and **1c** in chloroform at room temperature are 0.4, 5.5 and 23 mM, respectively.

Table 1 CT absorption and association constants (K_a) in chloroform at 25 °C

Donor	Acceptor	λ_{max}/nm	$\varepsilon/10^3$ M^{-1} cm^{-1}	K_a/M^{-1} [b]
1a	DNF	455[a]	—	815 ± 65
	TNF	505	1.09	273 ± 11
	TNFMN	620	1.36	305 ± 3[c]
	TCNQ	710	1.44	1500 ± 120
	DMTCNQ	675	1.08	340 ± 5[c]
1b	DNF	490[a]	—	2830 ± 130[c]
	TNF	540	1.01	544 ± 44
	TENF	620	0.77	302 ± 2[c]
		500[a]	—	
1c	DNF	490[a]	—	1760 ± 210
	TNF	535	1.07	565 ± 23
	TENF	615	0.96	223 ± 16
	TNFMN	665	1.67	595 ± 11[c]
	TCNQ	765	1.24	4810 ± 390
	DMTCNQ	730	0.91	774 ± 4[c]
A	DNF	480[a]	—	< 1
	TNF	540	1.20	5 ± 0[c]
		450	1.43	
	TENF	615	1.26	10 ± 0[c]
		500	1.38	
	TNFMN	660	1.36	20 ± 0[c]
	TCNQ	790	2.01	2 ± 0[c]
	DMTCNQ	745	1.26	3 ± 0[c]
MA	TNF	575	1.19	10.4 ± 0.4
		480	1.29	
	TCNQ	860	1.73	3.6 ± 1.5
DMA	TNF	605	1.31	12.8 ± 1.0
		505	1.56	

[a] Shoulder. [b] The standard deviations derived from repeated runs unless otherwise noted. [c] The conditional standard deviations from the least-squares curve-fitting (J. R. Long and R. S. Drago, *J. Chem. Educ.*, 1982, **59**, 1037).

Results and discussion

Thermodynamic properties of the complexes

CT Absorption and association properties in chloroform at 25 °C are summarised in Table 1.‡ The bis-anthracene host compounds have binding constants of from one order [*e.g.* **1a**–TNF and 9-methylanthracene (MA)–TNF] to three orders (*e.g.* **1a**–TCNQ and MA–TCNQ) of magnitude larger than those of the mono-anthracene derivatives for the same acceptors. The bis-donors are thus effective in forming CT complexes in solution.

In the case of **1a**, the association constants range from 270 M^{-1} for TNF to 1.5 × 10^3 M^{-1} for TCNQ. The alkylated derivatives, **1b** and **1c**, are similar but a little better than **1a** in its ability to bind to acceptors. The slight increase in the affinity by alkylation of the anthracene rings can be ascribed to the electron-donating nature of the alkyl group, which can be seen in the red-shift of the CT absorption band from those of **1a** as discussed later. MA associates more strongly than anthracene (A) with acceptors for the same reason.

The association free energies are plotted against the electron affinity (E_A) of acceptors in Fig. 1. The trend in the selectivity of the bis-donors is quite different from that of mono-donors. The binding constant for the bis-donors goes through minimum at TENF. Temperature-variation measurements were carried out and thermodynamic parameters (ΔH and $T\Delta S$) were determined better to understand the observed selectivity (Table 2).

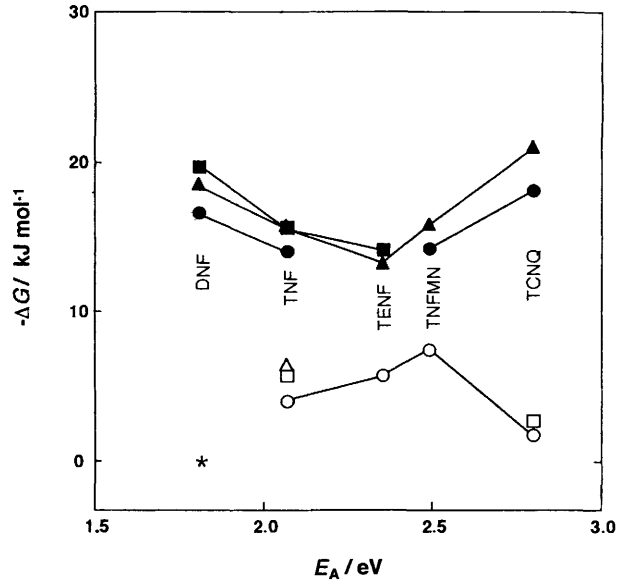


Fig. 1 Plot of the the complex stability ($-\Delta G$) of CT complexes of A (○), MA (□), DMA (△), **1a** (●), **1b** (■) and **1c** (▲) against E_A of acceptors. The asterisk (*) indicates the upper limit estimation for complexation of MA with DNF.

The complexations are exclusively exothermic and enthalpy-driven with a negative entropic contribution. The values of $-\Delta H$ of complexes **1a**–**1c** are two or more times those of corresponding mono-donors for the same acceptors. The increase in $-\Delta H$, up to the twofold value, can be ascribed to simultaneous electron donor–acceptor interactions[11,12] with two anthryl residues. Possible causes for the remainder of the

‡ The accurate values of K_a of **1a** and TENF could not be determined since precipitation occurred during the measurement, although the apparent association constant immediately after mixing of the components has been reported previously.[9] Although the K_a of **1a** and DNF was reported to be very small,[9] careful reinvestigation gave the value reported here.

Table 2 Thermodynamic parameters and standard deviations for CT complexes in $CHCl_3$ at 25 °C

Donor	Acceptor	$-\Delta G$/kJ mol^{-1}	$-\Delta H$/kJ mol^{-1}	$-T\Delta S$/kJ mol^{-1}
1a	DNF	16.6 ± 0.2	23.2 ± 2.5	6.6 ± 2.5
	TNF	13.9 ± 0.1	31.7 ± 0.8	17.8 ± 0.8
	TCNQ	18.1 ± 0.2	39.1 ± 2.3	21.0 ± 2.3
1b	TNF	15.6 ± 0.2	36.0 ± 2.1	20.5 ± 2.1
1c	DNF	18.5 ± 0.3	28.0 ± 3.4	9.5 ± 3.4
	TNF	15.7 ± 0.1	36.5 ± 1.1	20.8 ± 1.1
	TENF	13.2 ± 0.2	37.0 ± 2.6	23.8 ± 2.6
	TCNQ	21.0 ± 0.2	46.2 ± 1.9	25.2 ± 1.9
MA	TNF	5.8 ± 0.1	11.0 ± 0.9	5.2 ± 0.9
	TCNQ	3.2 ± 0.1	10.9 ± 1.1	7.8 ± 1.1
DMA	TNF	6.3 ± 0.2	17.9 ± 2.0	11.6 ± 2.1

gain in enthalpy are a stronger donor–acceptor interaction with the acceptor being fixed more tightly by the anthryl arms in the cleft, and different solvation or conformational energies in the bis-donor and mono-donor systems. From the present data, these possibilities cannot be distinguished.

The values of $-\Delta H$ for **1b** and **1c** are 5–7 kJ mol^{-1} larger than those of **1a**, corresponding to the increase in π-basicity of the anthracene rings upon alkyl substitution. A decrease in $T\Delta S$ is also observed of *ca.* 3 kJ mol^{-1}. The overall effect is a slight increase ($\Delta\Delta G$ *ca.* 2–3 kJ mol^{-1}) in the stability of the complexes of **1b** and **1c** compared with that of **1a**.

As the acceptor strength is increased, the gain in enthalpy becomes bigger, while entropy exerts the opposite effect. The overall stability and selectivity is a compromise of these opposing effects. A plot of ΔH *versus* $T\Delta S$ is shown in Fig. 2 for all the data in Table 2 to clarify the trends of the compensatory behaviour for the complaxation processes. In the case where the acceptor is DNF or TCNQ, the data are on a straight line, the slope of which is 0.9. The near-unity slope indicates that the gain in enthalpy by a stronger donor–acceptor interaction with stronger acceptors is largely offset by the unfavourable entropy decrease. Stronger acceptors have only a marginal advantage in binding to the bis-donors. The major factor that determines the selectivity is not the strength of the acceptor. Rather, deviations from the straight line in the direction of unfavourable association is important, and these are observed for the complexes of bis-donors with TNF and TENF, indicated by black circles in Fig. 2. This is interpreted in terms of structural restriction of these complexes due to nitro residues in the bay region of fluorenone, which are assumed to be located deeper in the cleft as discussed later in relation to NMR spectroscopy. Thus, the bis-donors are more sensitive to the structure of the acceptor and are able to distinguish subtle differences in shape of the guests.

It is apparent from Fig. 2 that the plot for bis-donors is shifted upward (or to the left) from that for mono-donors. For the same acceptor, the enthalpy gain for the bis-donors is two or more times that for mono-donors. With the upward shift of the regression line, the bis-donors gain this enthalpy with a smaller entropy decrease than the mono-donors would do. This is the origin of the 'bis' effect, *i.e.* enhanced binding to acceptors, conferred by the preorganization of the host.

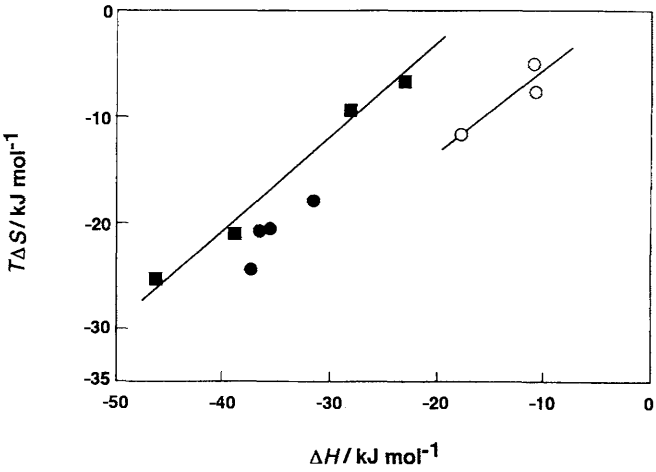


Fig. 2 Enthalpy–entropy compensation plot for the complexation of bis-donors with DNF, TCNQ (■), TNF and TENF (●), and mono-donors (○)

CT Absorption

For all donors investigated here, transition energies, $h\nu_{CT}$, corresponding to CT absorption maxima,§ are linearly dependent on E_A[14–16] of the acceptors (Fig. 3). Furthermore, the slope of the straight lines is *ca.* −1. These results indicate that these CT complexes are of weak b_π–a_π type,[17] for which the charge transfer in the ground state can be neglected.

Compared with the monomer model compounds that are assumed to be of the same ionization potential, *i.e.* **1a** with MA, and **1b** and **1c** with 9,10-dimethylanthracene (DMA), the CT transitions of the bis-donor complexes are shifted to higher energy by 30 kJ mol^{-1}. This value is of about the same order as the increase in the ground-state stabilization of the bis-donors from that of mono-donors. For weak CT complexes, the CT energy can be expressed approximately as eqn. (1),[4,17] where G_1

$$h\nu_{CT} = I_D - E_A - \Delta H - G_1$$

is the stabilization energy from the formation of the dative form from the free ions in the excited state and I_D is the ionization energy of donor. The higher energy shift of transition indicates that the stabilization in the ground state ($-\Delta\Delta H$) is bigger than that in the excited state (ΔG_1) for the same set of I_D and E_A. The values of G_1 can be calculated from the above equation with known values of I_D,[16] E_A[14–16] and the data reported here. Although an accurate estimation is difficult owing to uncertainty in I_D of the bis-donor,¶ the values of G_1 for bis-donors and mono-donors are calculated to be more or less constant around 300 kJ mol^{-1}. This is because G_1 is a term

§ When two CT bands appeared due to two closely located vacant orbitals of the electron acceptor,[13] the first CT bands of lower energy are plotted.

¶ The value of I_D for MA was used for **1a** and that of DMA was used for **1b** and **1c**. The values of I_D for MA and DMA were estimated to be greater than that of A (7.45 eV[16]) by 1.5 and 3.0 eV, respectively from the λ_{max} of the CT absorption with TNF (Fig. 3).

Table 3 Chemical shifts (italic) and CIS values of **1c**

Acceptor	aq2	aq3	aq4	an1	an4	an2,3	CH_2O	CH_2R
	7.44	*7.55*	*7.89*	*8.31*	*8.15*	*7.16–7.31*	*5.98*	*3.48*
DNF	−0.28	−0.29	−0.17	+0.54	+0.67	+0.24	+0.32	+0.57
TNF	−0.21	−0.23	−0.14	+0.48	+0.60	+0.23	+0.38	+0.56
TENF	−0.27	−0.31	−0.21	+0.68	+0.74	+0.20	+0.52	+0.60
TCNQ	−0.23	−0.22	−0.12	+0.30	+0.22	−0.19	+0.27	+0.30

Table 4 Chemical shifts (italic) and CIS values of fluorenones derivatives and TCNQ for complexation with **1c**

Acceptor	H-1	H-3	H-4	H-5	H-6	H-8
DNF	*8.60*	*8.53*	*7.88*	*7.88*	*8.53*	*8.60*
	+0.80	+1.55	+1.08	+1.08	+1.55	+0.80
TNF	*8.84*	*9.04*		*8.38*	*8.59*	*8.69*
	+0.60	+0.84		+0.98	+1.04	+0.97
TENF	*8.92*	*9.05*			*9.05*	*8.92*
	+0.93	+1.01			+1.01	+0.93
TCNQ	*7.56* (H-2,3,5,6)					
	+1.29					

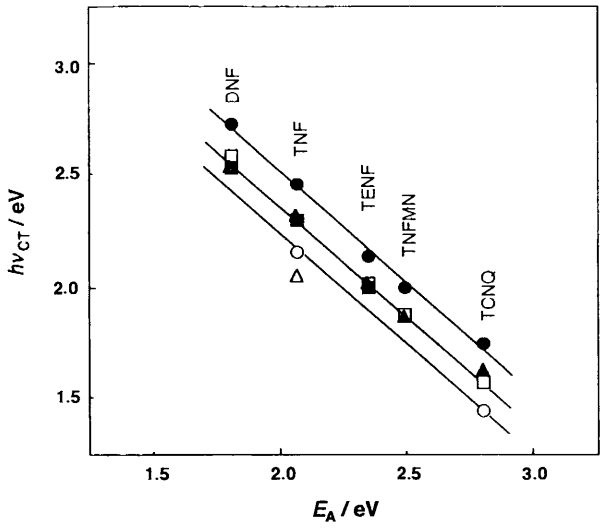


Fig. 3 Relationship between E_A of acceptors and the transition energy of CT absorption by complex of A (□), MA (○), DMA (△), **1a** (●), **1b** (■) and **1c** (▲)

composed mainly of the Coulomb stabilization energy of the charge-transferred state and is a function of the separation of donor and acceptor in the complex. In other words, that these values are similar indicates that the donor–acceptor separations are similar in the bis- and mono-donor complexes.

Solution structure of the complexes

For the complexes of **1c** with DNF, TNF, TENF and TCNQ, the limiting CIS values of the ^1H NMR spectra were determined, the results being summarized in Tables 3 and 4.‖ The following discussion indicates the highly oriented nature of the complex in line with the structure of the acceptor.

The protons of the guests and the anthryl moieties of the host, except AnH-2 and -3 in the complex with TCTQ, are shifted upfield and those of the anthraquinone spacer experience downfield shifts. This trend and the CIS values are in agreement with the result obtained previously for the complex **1a**–TNF, from which we concluded that TNF was sandwiched between the two anthryl groups, based on quantitative calculations of the ring-current effect.[9]

For all acceptors, the upfield shifts of A-CH_2R are larger than A-CH_2O by varing degrees from 0.03 ppm for TCNQ to 0.25 ppm for DNF. This suggests that the guest skeleton is displaced somewhat from the centre of the anthracene ring away from the spacer. The observation that CIS values for H-3, H-4, H-5 and H-6 of nitrofluorenones are always greater than those for H-1 and H-8 suggests that the concave side (bay region) of the fluorenones is located closer to the centre of anthracene and deeper into the cleft than the convex side (Fig. 4).

For complexes of TNF, a more subtle feature of the complex structure can be deduced from the data, since all of the protons of TNF are discernible owing to the dissymmetrical nature of the molecule. The observation that CIS values for H-1 and H-3 are smaller than those for H-5, H-6 and H-8 suggests that the fused ring of TNF bearing one nitro group is bound further into the cleft than the ring carrying two nitro groups [Fig. 4(*b*)]. This is ascribable to the steric hindrance of the nitro group at the 4-position. This structural restriction may be the reason for the large increase in $-T\Delta S$ upon complexation, as discussed earlier. This orientation is also observed for the complex **1a**–TNF, in sharp contrast with Zimmerman's molecular tweezers.[7b]

The downfield shift of H-2 and H-3 of the anthryl group observed only for the complex with TCNQ is due to the nitrile groups. This suggests that TCNQ is oriented with its long axis parallel to the long axis of the anthracene ring [Fig. 4(*d*)]. This is in fact the case in the solid-state of the complex **1a**–TCNQ, which was revealed by single-crystal X-ray analysis.[10]

Conclusions

Here we described the characterization of the 'sandwich' CT complexes with bis-anthracene donor and aromatic acceptors. In particular, the origin of the strong association with and the apparently complicated selectivity towards guest acceptors has been revealed by a thermodynamic analysis of the complexation processes, which is summarized as follows. The association constants are much larger due to sandwich-type association.

‖ Self-association of **1a** does not occur at least up to 0.4 mM, the maximum soluble concentration, in chloroform, since the chemical shifts are independent of its concentration. The plots of chemical shift against the ratio of the amount of the complex to the total amount of the donor or acceptor calculated from the UV–VIS data gave good straight lines, which indicates good agreement between NMR and UV–VIS experiments on the association processes.

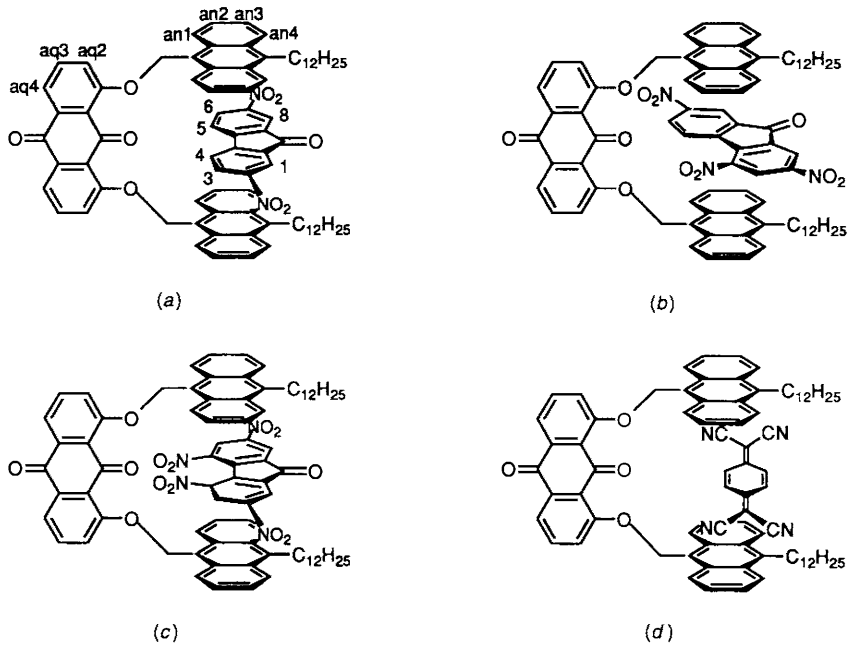


Fig. 4 Proposed structures of the 'sandwich' complexes of bis-donor **1c** with (*a*) DNF, (*b*) TNF, (*c*) TENF and (*d*) TCNQ in chloroform solution, based on CIS values of ^{1}H NMR and other evidence

This gain in the free energy upon association is due to enthalpic gain, which is two or more times those for mono-donor systems, accompanied by a smaller entropy loss effected by the preorganization of the host. Selectivity is mainly determined not by the electron affinity, which correlates only with the enthalpy term, but by steric features of the guest acceptors.

The other features of the CT complexes are: (1) they are of weak b_π–a_π type; (2) λ_{max} is blue-shifted mainly because of a larger ground-state stabilization than in the monomeric counterpart and (3) the guest acceptor is highly oriented in the cleft.

Experimental

Physical measurements

^{1}H NMR spectra (270 MHz) were recorded on a JEOL-GX270 or -EX270 spectrometer in $CDCl_3$ solutions with Me_4Si as an internal standard. CIS Values of ^{1}H NMR signals were determined by extrapolating the chemical shifts to the 100% complexation as described previously.[9] FTIR spectra were recorded on a Perkin-Elmer 1600 spectrometer. Electronic spectra were measured by using a JASCO Ubest-50 or Shimadzu UV 2200 spectrophotometer. Absorbance of the CT band of the complexes was plotted as a function of [acceptor] with [donor] being kept constant in chloroform solution. Association constants K_a were evaluated by the least-squares curve-fitting procedure as described previously.[9] Thermodynamic parameters were obtained by plotting K_a as a function of temperature from 10 °C to 45 °C.

Materials

Chloroform for spectroscopic measurements was refluxed and distilled over P_2O_5 under nitrogen. Water was purified by means of a Millipore Milli-Q Labo system. Other chemicals were used directly as received.

Chloromethylation of 9-alkylanthracene[18] gave 9-chloromethyl-10-alkylanthracene.[19] The synthesis of **1a** has been reported previously and **1b** and **1c** were prepared in a similar way under phase-transfer conditions.[9]

1,8-Bis[(10-butylanthracen-9-yl)methoxy]-9,10-anthraquinone (1b)

Recrystallized from CH_2Cl_2–hexane as yellow needles (23%) (Found: C, 85.5; H, 5.8. $C_{52}H_{44}O_4$ requires C, 85.2, H, 6.1%); mp 210 °C (decomp.); *m/z* 732 (M^+); $\delta_H(CDCl_3)$ 1.03 (6 H, t, CH_3), 1.6–1.9 [8 H, $(CH_2)_2$], 3.52 (4 H, t, $anCH_2R$), 6.02 (4 H, s, CH_2O), 7.15–7.35 (8 H, anH-2,3), 7.46 (2 H, d, aqH-2), 7.57 (2 H, t, aqH-3), 7.90 (2 H, d, aqH-4), 8.17 (4 H, d, anH-4), 8.32 (4 H, d, anH-1); ν_{max}(KBr)/cm^{-1} 744, 961, 1223, 1269, 1313, 1586, 1672 and 2955.

1,8-Bis[(10-dodecylanthracen-9-yl)methoxy]-9,10-anthraquinone (1c)

Recrystallized from CH_2Cl_2–hexane as a yellow solid (35%) (Found: C, 85.2; H, 7.9. $C_{68}H_{76}O_4$ requires C, 85.3, H, 8.0%); mp 165 °C (decomp.); $\delta_H(CDCl_3)$ 0.89 (6 H, t, CH_3), 1.2–1.8 [40 H, $(CH_2)_{10}$], 3.48 (4 H, t, $anCH_2R$, J = 7.4 Hz), 5.98 (4 H, s, CH_2O), 7.16–7.31 (8 H, anH-2,3), 7.44 (2 H, d, aqH-2, J = 8.1 Hz), 7.55 (t, 2 H, aqH-3, J = 7.9 Hz), 7.89 (2 H, d, aqH-4, J = 6.4 Hz), 8.15 (4 H, d, anH-4, J = 9.0 Hz), 8.31 (4 H, d, anH-1, J = 8.6 Hz); ν_{max}(KBr)/cm^{-1} 742, 962, 1233, 1267, 1314, 1456, 1585, 1670 and 2850.

Acknowledgements

This work was partly supported by a Grant-in Aid for Scientific Research from the Ministry of Education, Science and Culture.

References

1 H. A. Benesi and J. H. Hildebrand, *J. Am. Chem. Soc.*, 1949, **71**, 2703.
2 R. S. Mulliken, *J. Am. Chem. Soc.*, 1952, **74**, 811.
3 M. R. Bryce, *Chem. Soc. Rev.*, 1991, **20**, 355.
4 C. J. Bender, *Chem. Soc. Rev.*, 1986, **15**, 475.
5 (*a*) J.-M. Lehn, *Angew. Chem., Int. Ed. Engl.*, 1988, **27**, 89; (*b*) 1990, **29**, 1304.
6 J. Otsuki and K. Araki, *Seisankenkyu*, 1992, **44**, 469.
7 (*a*) S. C. Zimmerman and C. M. VanZyl, *J. Am. Chem. Soc.*, 1987, **109**, 7894; (*b*) S. C. Zimmerman, C. M. VanZyl and G. S. Hamilton, *J. Am. Chem. Soc.*, 1989, **111**, 1373; (*c*) S. C. Zimmerman, M. Mrksich and M. Baloga, *J. Am. Chem. Soc.*, 1989, **111**, 8528; (*d*) S. C. Zimmerman and K. W. Saionz, *J. Am. Chem. Soc.*, 1995, **117**, 1175.
8 (*a*) P. L. Anelli, P. R. Ashton, R. Ballardini, V. Balzani, M. Delgado, M. T. Gandolfi, T. T. Goodnow, A. E. Kaifer, D. Philp, M. Pietraszkiewicz, L. Prodi, M. V. Reddington, A. M. Z. Slawin, N. Spencer, J. F. Stoddart, C. Vicent and D. J. Williams, *J. Am. Chem. Soc.*, 1992, **114**, 193; (*b*) D. B. Amabilino, P. R. Ashton, C. L.

Brown, E. Córdova, L. A. Godínez, T. T. Goodnow, A. E. Kaifer, S. P. Newton, M. Pietraszkiewicz, D. Philp, F. M. Raymo, A. S. Reder, M. T. Rutland, A. M. Z. Slawin, N. Spencer, J. F. Stoddart and D. J. Williams, *J. Am. Chem. Soc.*, 1995, **117**, 1271.
9 J. Otsuki, L.-C. Chiang, S.-H. Lee, K. Araki and M. Seno, *Supramol. Chem.*, 1993, **2**, 25.
10 J. Otsuki, T. Oya, S.-H. Lee and K. Araki, *J. Chem. Soc., Chem. Commun.*, 1995, 2193.
11 H.-J. Schneider, *Angew. Chem., Int. Ed. Engl.*, 1991, **30**, 1417.
12 C. A. Hunter and J. K. M. Sanders, *J. Am. Chem. Soc.*, 1990, **112**, 5525.
13 S. Iwata, J. Tanaka and S. Nagakura, *J. Am. Chem. Soc.*, 1966, **88**, 894.
14 J. E. Kuder, J. M. Pochan, S. R. Turner and D. F. Hinman, *J. Electrochem. Soc.*, 1978, **125**, 1750.
15 R. C. Wheland and J. L. Gillson, *J. Am. Chem. Soc.*, 1976, **98**, 3916.
16 *Kagaku Binran Kisohen II*, 4th edn., ed. Chem. Soc. Jpn., Maruzen, Tokyo, 1993 (a Japanese handbook of chemistry).
17 R. S. Mulliken and W. B. Person, *Molecular Complexes, A Lecture and Reprint Volume*, Wiley, New York, 1969.
18 F. van de Griendt and H. Cerfontain, *J. Chem. Soc., Perkin Trans. 2*, 1980, 13.
19 F. H. C. Stewart, *Aust. J. Chem.*, 1960, **3**, 478.

Paper 5/06830D
Received 16*th October* 1995
Accepted 24*th November* 1995