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Syntheses and Properties of Di-, Tri-, and Tetracyclopropyltropylium and Di- and Tri-*t*-butyltropylium Ions

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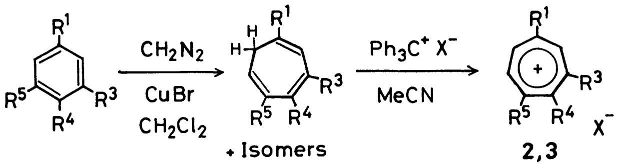
The polysubstituted tropylium ions having cyclopropyl or *t*-butyl groups at the ring positions with the least steric hindrance, *i.e.* 1,3- and 1,4-dicyclopropyltropylium, 1,3- and 1,4-di-*t*-butyltropylium, 1,3,5-tricyclopropyl- and 1,3,5-tri-*t*-butyltropylium and 1,2,4,6-tetracyclopropyltropylium ions (**4**), were synthesized, and their properties were compared with the known monosubstituted and unsubstituted cations. The ^{1}H and ^{13}C NMR spectra for the cyclopropyl derivatives and the ^{13}C NMR spectra for the *t*-butyl derivatives exhibited a gradual upfield shift for the seven-membered ring signals upon consecutive substitution. Accordingly, for the *t*-butyl derivatives, the pK_{R^+} values were found to linearly increase upon introduction of each substuent; for the cyclopropyl derivatives, a larger extent of the pK_{R^+} increase was observed with each substitution, and the pK_{R^+} of the tetrasubstituted derivative **4** amounted to 9.10 (50% aq MeCN, 25 °C), the highest value presently known for the hydrocarbon cations having the tropylium unit, although the cumulative substituent effect deviated from the linear additivity correlation as the substituent number increased. The substituent effects upon the reduction potential and the CT transition energy (pyrene as a donor) were also examined and shown to have the same tendency in general.

The stabilization of the carbocation by the cyclopropyl (c-Pr) group is now widely recognized.[1] Especially for the tropylium ion as the representative Hückel aromatic cation, our previous study on pK_{R^+} and one-electron reducibility indicated that the σ-conjugative stabilization by the c-Pr group is more than twice as effective as the stabilization by the *t*-butyl (*t*-Bu) group with its purely inductive electron donation, while the π-conjugative stabilization of the phenyl group was no more observable owing to the *ortho*-hydrogen repulsion.[2]

On the other hand, the detailed study on the reducibility of a series of polymethyltropylium ions revealed that the additivity of the substituent effect upon cation stability holds when no severe steric congestion is present around the tropylium ring, *i.e.* when the number of substituents does not exceed more than five.[3] Thus, we synthesized the tropylium ions substituted with two to four c-Pr groups and with two and three *t*-Bu groups at the ring positions where the effect of steric repulsion is minimized, and examined the additivity of the electronic effect of these substituents upon cation stability.

Syntheses. The 1,3- and 1,4-disubstituted (**2**) and 1,3,5-trisubstituted tropylium ions (**3**) each having the c-Pr (**2a**, **2b**, and **3a**) or *t*-Bu groups (**2c**, **2d**, and **3b**[4])) were synthesized as shown in Scheme 1, by the use of the conventional method involving the CuBr-catalyzed ring expansion of the substituted benzenes with diazomethane, followed by hydride abstraction.

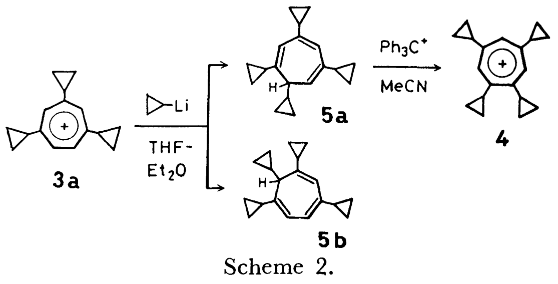


	R^1	R^3	R^4	R^5	X
$\mathbf{2a}\cdot X^-$	c-Pr	c-Pr	H	H	BF_4
$\mathbf{2b}\cdot X^-$	c-Pr	H	c-Pr	H	BF_4
$\mathbf{2c}\cdot X^-$	*t*-Bu	*t*-Bu	H	H	ClO_4
$\mathbf{2d}\cdot X^-$	*t*-Bu	H	*t*-Bu	H	ClO_4
$\mathbf{3a}\cdot X^-$	c-Pr	c-Pr	H	c-Pr	BF_4
$\mathbf{3b}\cdot X^-$	*t*-Bu	*t*-Bu	H	*t*-Bu	ClO_4

Scheme 1.

For the synthesis of the tetracyclopropyltropylium ion (**4**), we adopted a cation-anion combination reaction of the trisubstituted cation **3a** with cyclopropyllithium at −70 °C as shown in Scheme 2. 1,3,5,7-Tetracyclopropylcycloheptatriene (**5a**), which was isolated in 41% yield, was then treated with the trityl cation to give the 1,2,4,6-tetracyclopropyltropylium ion (**4**) in 85% yield. The 1,3,6,7-tetrasubstituted derivative **5b** with higher steric hindrance was isolated only in 8% yield.

Properties. The physical and spectral properties of the newly synthesized salts of the cations **2a**—**d**, **3a**, **b**, and **4** are shown in Table 1, together with the data for the unsubstituted (**6**) and monosubstituted cations ($R-C_7H_6^+$: R=c-Pr (**1a**), *t*-Bu (**1b**)) for the purpose of comparison.



Scheme 2.

Among these data, it is to be noted that in the ^{1}H NMR spectra for a series of c-Pr-substituted cations the signal for the tropylium-ring protons, which appears as a somewhat broadened singlet except for the cation **4**, is gradually shifted upfield with higher substitution. This upfield shift is supposed to reflect mostly the electronic effect of the increasing number of c-Pr substituents delocalizing the positive charge away from the cationic ring, in addition to the anisotropic ring-current effect of the c-Pr ring.[5] A similar general trend

TABLE 1. PHYSICAL AND SPECTRAL PROPERTIES OF THE SALTS OF UNSUBSTITUTED (**6**) AND SUBSTITUTED TROPYLIUM IONS (**1**, **2**, **3**, AND **4**)

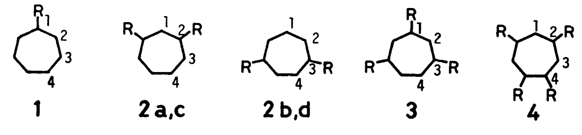
Tropylium salt	Mp (decomp) θ_m/°C	UV (MeCN) λ_{max}/nm (log ε)	^{1}H NMR (CD_3CN) δ from Me_4Si
6·BF_4^-	≈200	219(4.61) 275(3.55)	9 29 (s)
c-Pr-substituted cations			
1a·BF_4^-[a)]	58.2—60.0	247(4.52) 328(4.11)	8.83 (s, 6H, $-CH^+-$) 2.85—2.45 (m, 1H, c-Pr-H_α) 2.05—1.41 (m, 4H, c-Pr-H_β)
2a·BF_4^-	≈185[b)]	230(4.16) 274(4.38) 329(4.11)	8.38 (s, 5H, $-CH^+-$) 2.76—2.30 (m, 2H, c-Pr-H_α) 2.05—1.30 (m, 8H, c-Pr-H_β)
2b·BF_4^-	156.3—156.6	244(4.49) 348(4.35)	8.37 (s, 5H, $-CH^+-$) 2.66—2.23 (m, 2H, c-Pr-H_α) 1.90—1.21 (m, 8H, c-Pr-H_β)
3a·BF_4^-	189.5—191.0	279(4.55) 343(4.24)	7.96 (s, 4H, $-CH^+-$) 2.68—2.16 (m, 3H, c-Pr-H_α) 1.67—1.15 (m, 12H, c-Pr-H_β)
4·ClO_4^-	99.5—100.0	285(4.81) 342(4.38)	7.73 (d, J=1.3 Hz, 2H, $-CH^+-$) 7.64 (t, 1H, $-CH^+-$) 2.86—2.20 (m, 4H, c-Pr-H_α) 1.63—1.04 (m, 16H, c-Pr-H_β)
t-Bu-substituted cations			
1b·ClO_4^-[c)]	179.0—180.0	223(4.50)[d)] 293(3.69)	9.4—9.1 (m, 6H, $-CH^+-$)[e)] 1.70 (s, 9H, *t*-Bu)
2c·ClO_4^-	204.0	234(4.50)[d)] 291(3.80)	9.6—8.6 (m, 5H, $-CH^+-$)[e)] 1.66 (s, 18H, *t*-Bu)
2d·ClO_4^-	172.0—173.0	227(4.60)[d)] 305(3.90)	9.3—8.6 (m, 5H, $-CH^+-$)[e)] 1.66 (s, 18H, *t*-Bu)
3b·ClO_4^-	195.5—196.0	240(4.61)[d)] 299(3.90) 307sh (3.84)	9.35 (s, 2H, $-CH^+-$)[e)] 9.13 (s, 2H, $-CH^+-$) 1.69 (s, 27H, *t*-Bu)

a) Ref. 2b. b) Charring without showing a clear mp. c) Ref. 2a. d) In 10% HCl. e) In CF_3CO_2H.

TABLE 2. ^{13}C NMR SPECTRAL DATA FOR THE UNSUBSTITUTED (**6**) AND SUBSTITUTED TROPYLIUM IONS (**1**, **2**, **3**, AND **4**)

Cation[a)]	^{13}C NMR chemical shift, δ (CD_3CN)					
	C-1	C-2	C-3	C-4	Substituent C-α	Substituent C-β
6	156.2	—	—	—	—	—
c-Pr-substituted cations						
1a	182.7	152.3[b)]	152.5[b)]	151.1	25.1	21.5
2a	147.6	177.3	147.5[b)]	149.2[b)]	24.5	19.5
2b	149.8	147.0[b)]	177.3	148.6[b)]	23.5	19.4
3a	173.4	143.9[b)]	172.6	145.3[b)]	24.3[c)]	18.2[c)]
					23.3[d)]	17.6[d)]
4	140.9	171.8	142.0	169.2	23.7[e)]	17.5[e)]
					21.6[f)]	12.7[f)]
t-Bu-substituted cations						
1b	184.0	153.9	154.1	154.3	42.2	31.5
2c	150.1	181.2	152.1	152.4	42.7	31.5
2d	152.3	151.9	181.4	151.3	41.5	31.2
3b	179.2	148.4	178.8	150.5	43.3[c)]	31.7[c)]
					42.1[d)]	31.4[d)]

a) The numbering systems are as follows:



b) These values may be interchangeable. c) At C-1. d) At C-3. e) At C-2. f) At C-4.

Table 3. Data of pK_{R^+}, reduction potential, and CT band with pyrene as a donor, for the unsubstituted (**6**) and substituted tropylium ions (**1**, **2**, **3**, and **4**)

Cation	pK_{R^+} [a]	Red potential *vs.* Ag/Ag+ [b] V	CT band [c] λ_{max}/nm	CT band [c] $\lambda/10^4$ cm^{-1}
6	3.88	−0.51	540[d]	1.85
c-Pr-substituted cations				
1a	5.76	−0.64	526[e]	1.90
2a	7.56	−0.76	500—510	2.00—1.96
2b	7.63	−0.76	495—505	2.02—1.98
3a	8.72	−0.86	485—495	2.06—2.02
4	9.10	−0.94	476—490	2.10—2.04
t-Bu-substituted cations				
1b	4.57	−0.61	508[d]	1.97
2c	4.90	−0.70	503	1.99
2d	5.42	−0.72	490—510	2.04—1.96
3b	6.26	−0.84	480—500	2.08—2.00

a) Determined spectrophotometrically in H_2O–MeCN (1 : 1 by volume); Ref. 7. b) Cathodic peak potential determined with CV in MeCN at a scan rate of 0.1 V/s; cation 1 mM; supporting electrolyte (Bu_4NClO_4), 0.1 M; Ref. 7. c) Observed in 1,2-dichloroethane; cation (acceptor), 1 mM; pyrene (donor), 0.1 M; Ref. 7. d) Ref. 2a. e) Ref. 2b.

is observed for the ^{13}C NMR data shown in Table 2.

Compared with the case of c-Pr-substituted cations, the aromatic-ring proton signals in the ^1H NMR spectra of *t*-Bu derivatives do not exhibit any systematic upfield shift upon consecutive substitution, presumably due to the considerable steric compression effect of the bulky *t*-Bu groups. In the ^{13}C NMR spectra, however, the gradual upfield shift is again clearly observed for the ring-carbon signals, though the increment of the upfield shift upon each substitution is apparently smaller than that observed for a series of c-Pr derivatives.†

Based on these results of NMR measurements, it is now of particular interest to examine the additivity of the substituent effects of the c-Pr and *t*-Bu groups upon the cation stability expressed by the pK_{R^+} value. As shown in Table 3, the pK_{R^+} value increases upon consecutive c-Pr substitution and reaches the maximum value of 9.10 for the tetra-c-Pr derivative **4**. To our knowledge this is the highest pK_{R^+} value reported for the hydrocarbon cations having the tropylium unit.[6]

Also included in Table 3 are the data of reduction potentials determined by cyclic voltammetry (CV) and of charge-transfer (CT) band observed with pyrene as a π-donor. In our previous study,[2a,2b,3] the CT transition energy of various mono- and polysubstituted tropylium ions with pyrene as a donor was shown to exhibit a linear correlation with the one-electron reducibility of these cations in solution. For the present series of cations, a similar correlation seems to hold in general.

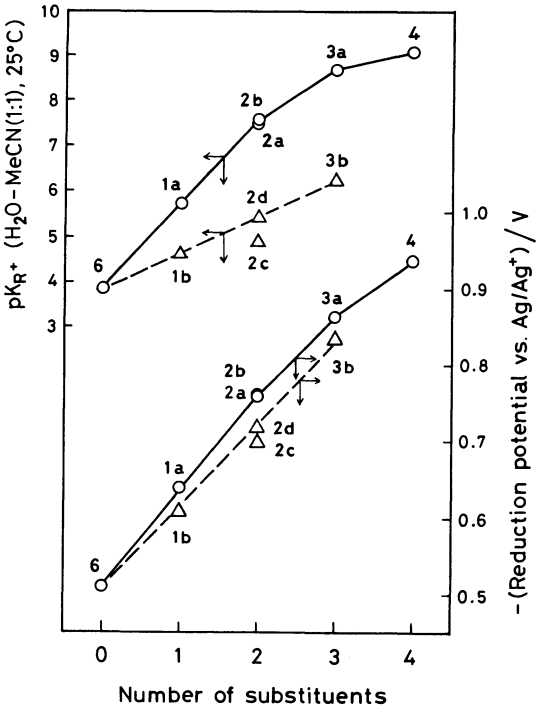


Fig. 1. Correlation of the pK_{R^+} and reduction potential with the number of substituent (○, c-Pr; △, *t*-Bu).

However, for the highly substituted derivatives, the CT absorption bands become much too weak to allow the accurate determination of the absorption maxima, presumably due to the steric congestion between the donor and acceptor.

Thus, the more precisely measurable values of pK_{R^+} (limit of precision, ± 0.05) and reduction potential (± 0.005 V) were plotted against the number of substituents to give the correlation shown in Fig. 1. From this plot is observed that, in contrast to the linear correlations obtained for the *t*-Bu derivatives, the pK_{R^+} of the c-Pr derivatives apparently deviates from the linear correlation line as the substituent number increases. This result seems to indicate that, for an aromatic cation like the tropylium ion, the additivity towards the cation stability holds for the substituents with the purely inductive electronic effect, whereas some saturation phenomenon exists for the cumulative effect of σ-conjugative substituents.†† The detailed discussion on the correlation between the pK_{R^+} and other indices corresponding to the electron affinity for a wider variety of stable cations will be made in a separate publication.[7]

[†] For the purpose of comparison, when we simply average the chemical shift values for the ring-carbons carrying no substituent, the following δ-values are obtained: **6**, 156.2; **1a**, 152.0; **2a**, 148.2; **2b**, 148.2; **3a**, 144.6; **4**, 141.6; **1b**, 154.1; **2c**, 151.8; **2d**, 151.7; **3b**, 149.5.

[††] This phenomenon would be attributed to the decrease in population of the c-Pr groups taking the bisected conformation as the cationic ring becomes less electron-demanding with higher substitution. Especially in the case of the cation **4**, the parallel conformation rather than the bisected one may be sterically favored for the two neighboring c-Pr groups at C-1 and C-2. However, these groups are apparently not fixed in such geometry, as judged from the small chemical-shift difference (*ca.* 0.1 ppm) between H-3,7 and H-5; the c-Pr groups in hexacyclopropylbenzene, for example, have been reported to be freely rotating in solution though fixed in the parallel conformation in the crystalline state.[8]

Experimental

General. Melting points are uncorrected. The elemental analyses were performed by the Microanalytical Center, Kyoto University, Kyoto. The IR and UV spectra were recorded on Hitachi 215 snd Hitachi 200-10 spectrometers, respectively. The ^{1}H NMR spectra were taken with a Hitachi R-24 spectrometer with Me_4Si as the internal standard. The ^{13}C NMR spectra were recorded on a JEOL FX-100 spectrometer operated in the Fourier transform mode.

Materials. The di- and tricyclopropylbenzenes were prepared from the corresponding di- and trivinylbenzenes following the method of Effenberger and Kurtz.[9] The di- and tri-*t*-butylbenzenes were prepared by the Friedel-Crafts *t*-butylation of benzene with *t*-butyl chloride catalyzed by $FeCl_3$ or $AlCl_3$. Other materials used were of the reagent grade quality unless otherwise noted.

*1,3-Dicyclopropyltropylium Tetrafluoroborate (**2a**·BF_4^-).* A 0.43 M solution of diazomethane in CH_2Cl_2 (50 ml), prepared from *N*-methyl-*N*-nitrosourea,[10] was added dropwise to a stirred solution of 1,3-dicyclopropylbenzene (1.87 g; 11.8 mmol) in CH_2Cl_2 (10 ml) in the presence of CuBr (0.55 g; 3.9 mmol) at 40 °C over 30 min. After refluxing for 20 min, the mixture was filtered and evaporated to give 2.20 g of the crude product, which was found to contain about 20% of olefinic compounds by the ^{1}H NMR analysis. The hydride abstraction of the crude product with trityl tetrafluoroborate (1.00 g; 3.03 mmol) in MeCN (3 ml) and CH_2Cl_2 (3 ml), followed by precipitation with dry ether and recrystallization from MeCN, afforded 0.374 g (12.3% yield based on dicyclopropylbenzene) of the product, the ^{13}C NMR spectrum of which indicated the formation of both the 1,3- (**2a**) and 1,4-dicyclopropyltropylium (**2b**) ions in a ratio of 2 : 1. The fractional recrystallization from MeCN repeated twice yielded 0.050 g of **2a**·BF_4^- as white crystals. Found: C, 60.47; H, 6.01%. Calcd for $C_{13}H_{15}BF_4$: C, 60.50; H, 5.86%.

*1,4-Dicyclopropyltropylium Tetrafluoroborate (**2b**·BF_4^-).* In exctly the same way, 1,4-dicyclopropylbenzene was allowed to react with two-fold excess of diazomethane in CH_2Cl_2. The subsequent hydride abstraction and recrystallization from MeCN afforded **2b**·BF_4^- as white crystals in 10.6% yield. Found: C, 60.34; H, 5.77%. Calcd for $C_{13}H_{15}BF_4$: C, 60.50; H, 5.86%.

*1,3,5-Tricyclopropyltropylium Tetrafluoroborate (**3a**·BF_4^-).* Similarly, **3a**·BF_4^- was synthesized from 1,3,5-tricyclopropylbenzene in 10.0% yield as white crystals. Found: C, 64.73%; H, 6.57%. Calcd for $C_{16}H_{19}BF_4$: C, 64.46; H, 6.42%.

*1,3-Di-*t*-butyltropylium Perchlorate (**2c**·ClO_4^-).* In the same way, **2c**·ClO_4^- was synthesized through the ring-expansion of 1,3-di-*t*-butylbenzene with diazeomthane in heptane, followed by hydride abstraction with trityl perchlorate in 7.0% yield as white crystals. Found: C, 59.32; H, 7.72%. Calcd for $C_{15}H_{23}ClO_4$: C, 59.50; H, 7.66%.

*1,4-Di-*t*-butyltropylium Perchlorate (**2d**·ClO_4^-).* Similarly, **2d**·ClO_4^- was synthesized from 1,4-di-*t*-butylbenzene in 9.2% yield as white crystals. Found: C, 59.32; H, 7.72%. Calcd for $C_{15}H_{23}ClO_4$: C, 59.50; H, 7.66%.

*1,3,5-Tri-*t*-butyltropylium Perchlorate (**3b**·ClO_4^-).* Similarly, **3b**·ClO_4^- was synthesized from 1,3,5-tri-*t*-butylbenzene in 4.5% yield as white crystals. Found: C, 63.32; H, 8.72%. Calcd for $C_{19}H_{31}ClO_4$: C, 63.59; H, 8.71%.

*1,2,4,6-Tetracyclopropyltropylium Perchlorate (**4**·ClO_4^-).* An ethereal solution (5 ml) of 0.48 M cyclopropyllithium (2.4 mmol), prepared from cyclopropyl bromide and Li, was added dropwise to a stirred suspension of **3a**·BF_4^- (0.309 g; 1.04 mmol) in dry THF (4 ml) cooled at −70 °C over 5 min. After stirring at −70 °C for 10 min, the temperature was slowly raised to room temperature over 1 h. The mixture was hydrolyzed and worked up in the usual manner to give 0.30 g of the crude product, which exhibited three main spots at R_f 0.60, 0.49, and 0.34 on an analytical TLC plate developed with hexane–benzene (9 : 1) over SiO_2 (Merck, GF_{254}). From the fraction with R_f 0.60, we isolated, by the use of preparative TLC over SiO_2 (Merck, F_{254}, pre-coated), 1,3,5,7-tetracyclopropylcycloheptatriene (**5a**) (0.107 g; 40.9%) as a colorless oil: IR (neat) ν 3080 m, 3005 m, 1621 m, 1460 w, 1425 w, 1018 m cm^{-1}; ^{1}H NMR (CCl_4) δ 6.02 (br s, 1H, H-4), 5.45 (br s, 1H, H-2), 4.91 (br d, 1H, H-6), 1.93—0.95 (m, 5H, H-7+c-Pr-H_α), 0.90—0.20 (m, 16H, c-Pr-H_β); ^{13}C NMR ($CDCl_3$) δ 144.7, 143.1, 136.8 (s×3, C-1,3,5), 123.7, 120.0, 117.5 (d×3, C-2,4,6), 47.2 (d, C-7), 18.2, 15.6, 14.9, 11.7 (d×4, c-Pr-C_α), 8.6, 7.6, 7.1, 6.4, 5.4, 5.3, 4.0, 3.9 (t×8, c-Pr-C_β). From the fraction with R_f 0.49, we also obtained the colorless oil (0.0215 g; 8.2%), which was assigned as 1,3,6,7-tetracyclopropylcycloheptatriene (**5b**) on the basis of the following spectral data; IR (CCl_4) ν 3085 m, 3005 m, 1620 w, 1456 w, 1426 w, 1018 m cm^{-1}; ^{1}H NMR (CCl_4) δ 6.12 (br d, 1H, H-4), 5.82 (br d, 1H, H-5), 5.55 (br s, 1H, H-2), 2.00—1.10 (br m, 5H, H-7+c-Pr-H_α), 1.00—0.30 (br m, 16H, c-Pr-H_β); ^{13}C NMR ($CDCl_3$) δ 141.4, 140.3, 140.0 (s×3, C-1,3,6), 122.1, 119.1, 118.5 (d×3, C-2,4,5), 50.4 (d, C-7), 19.5, 19.2, 18.1, 13.7 (d×4, c-Pr-C_α), 8.7—3.8 (partially overlapped eight peaks, c-Pr-C_β).

To a stirred solution of **5a** (0.0965 g; 0.383 mmol) in MeCN (1 ml) was added trityl perchlorate (0.0800 g; 0.234 mmol) in one portion. After stirring at room temperature for 3 h, dry ether (20 ml) was added to cause the formation of precipitates, which were then filtered and purified by reprecipitation from MeCN–ether to give **4**·ClO_4^- (0.0684 g; 83.4%) as off-white crystals. Found: C, 64.24; H, 6.69%. Calcd for $C_{19}H_{23}ClO_4$: C, 65.04; H, 6.61%.

pK_{R^+} Measurements. The pK_{R^+} values were determined in H_2O–MeCN (1 : 1 by volume) at 25 °C according to the spectrophotometric method described in our previous paper in detail.[11] The buffer solutions were made up by mixing 0.1 M citric acid and 0.1 M Na_2HPO_4 in H_2O–MeCN (1 : 1) (pH 3.0—8.2), and 0.01 M Na_2HPO_4 and 0.01 M Na_3PO_4, with 0.02 M Na_2CO_3 added in H_2O–MeCN (1 : 1) (pH 8.0—11.0). The pH values were read on a Horiba H pH meter calibrated with standard buffers before use.

Cyclic Voltammetry. The measurements were carried out in MeCN by the instruments and method previously reported.[11] As the reduction potential, we took the value of the cathodic peak potential of the voltammogram obtained at the scan rate of 0.1 V/s. The potential was determined against the reference electrode, Ag/0.01 M $AgNO_3$ with 0.1 M Bu_4NClO_4 in MeCN, and calibrated with $E_{1/2}$ of ferrocene added as an internal standard immediately after each measurement.

Charge-transfer Spectra. The spectra were taken in exactly the same way as previously reported,[2b] for the solution of 1×10^{-3} M cation (acceptor) and 0.1 M pyrene (donor) in 1,2-dichloroethane.

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