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CHIRAL MEMORY UNITS BASED ON DYNAMIC REDOX SYSTEMS WITH A DIBENZOXEPINONE SKELETON: DRASTIC CHANGE IN RACEMIZATION BARRIER AND ELECTROCHEMICAL BISTABILITY

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Dedicated to Professor Victor Snieckus on the occasion of his 77th birthday

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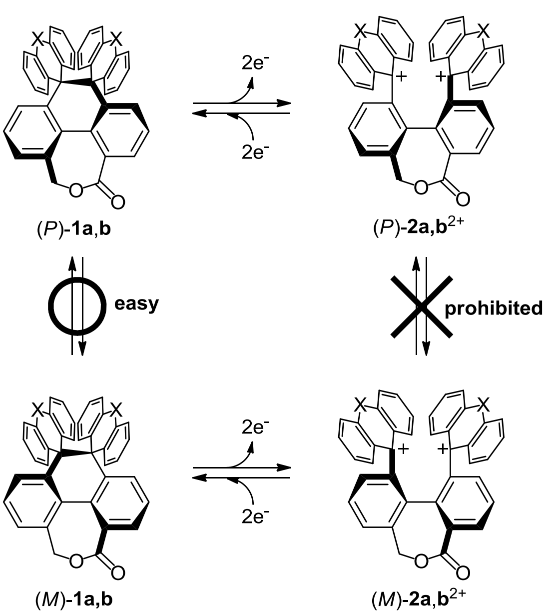
Abstract – The configuration of helical dicationic dyes $\mathbf{2}^{2+}$ with a dihydrodibenzoxepinone unit is stable, whereas the corresponding neutral electron donors **1** with a tetrahydrophenanthroxepinone skeleton easily undergo ring-flip. Thanks to their electrochemical bistability, electron exchange between **1** and $\mathbf{2}^{2+}$ is prohibited. Thus, the above electrochromic pairs $\mathbf{1}/\mathbf{2}^{2+}$ can serve as new members of less well-explored redox-based chiral-memory units.

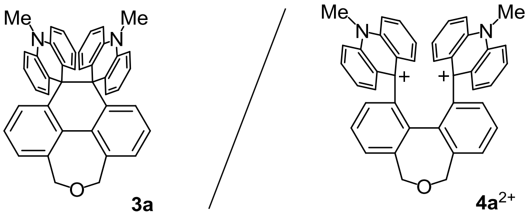
The intermolecular transmission of asymmetric information is the very important event in the field of supramolecular chirality.[1] Molecules that act as chiral-memory units play important roles in these phenomenon.[2] To ensure this function, the chiral unit should be able to adopt an easily-racemized state ("erasable/writable"-state), but must also be intentionally interconvertible with the non-racemized state ("memorizing"-state) under certain conditions. Switching by heating/cooling is successfully realized in the folded polymer chains with a helical structure[3] and some macrocyclic molecules.[4] However, much less has been reported on compounds whose interstate-switching[5] is achieved by electron transfer ("chiral redox memory") except our recent report based on the "dynamic redox pair"[6] of phenanthr[4,5-*cde*]oxepin-type donor **3a** and dibenz[*c*,*e*]oxepin-type dication $\mathbf{4a}^{2+}$.[7]

During our further studies toward the chiral memory units, we envisaged that more easily-accessible lactone analogues ($\mathbf{1}/\mathbf{2}^{2+}$) can serve as promising new entries (Scheme 1). Thus, the ring inversion of

4,6,10,11-tetrahydrophenanthr[4,5-*cde*]oxepin-4-one in **1** would occur easily at room temperature (the "erasable/writable"-state) whereas the ring flip of 5,7-dihydrodibenz[*c*,*e*]oxepin-5-one skeleton attached with two cationic chromophores at 1,11-positions in $\mathbf{2}^{2+}$ would be prohibited (the "memorizing"-state). As redox active chromophores, not only spiroacridan/acridinium (**a**) but also spiroxanthene/xanthenylium (**b**) were chosen for tuning the electric potentials at which the switching occurs (Table 1).[8] Here we report redox properties, configurational stability and electrochromic behavior of newly prepared lactone-based redox pairs ($\mathbf{1a,b}/\mathbf{2a,b}^{2+}$), that can be applicable for realizing chiral redox memories.



Scheme 1. Redox switching of racemization barrier (**a**: X = NMe; **b**: X = O)



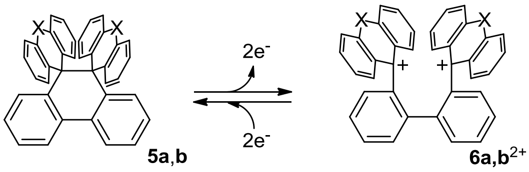


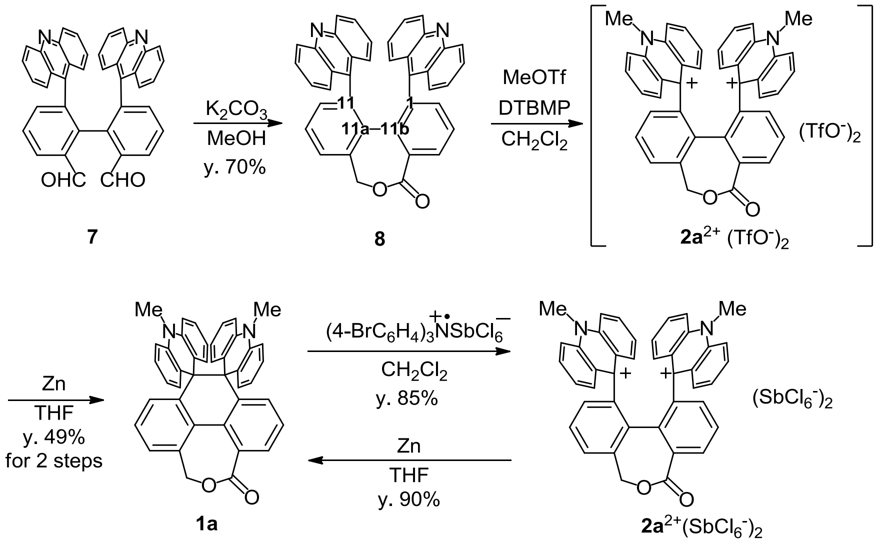
Table 1. Redox potentials measured in MeCN[a]

	E^{ox} of **5**	E^{red} of $\mathbf{6}^{2+}$
a: X = NMe	+0.18	-0.27
b: X = O	+1.02	+0.35

[a] *E*/V vs SCE, scan rate 100 mV s^{-1}, Pt electrode

Sterically congested hexaphenylethane-type molecule **1a** was planned to prepare via the corresponding bond-dissociated dication $\mathbf{2a}^{2+}$, and we first pursue generation of diacridinium $\mathbf{2a}^{2+}$. Thus, 9,9'-(6,6'-diformylbiphenyl-2,2'-diyl)diacridine (**7**) was derived from 2,2',6,6'-tetrabromobiphenyl over 3 steps in 52% yield as we reported previously.[9] Upon treating **7** with K_2CO_3 in MeOH, the Tishchenko reaction took place very smoothly[10] to give lactone **8**[11] in 70% yield. According to the X-ray analysis,[12] the 5,7-dihydrodibenz[*c*,*e*]oxepin-5-one skeleton in **8** adopts a deeply twisted geometry as expected, and the torsion angle of C^1-C^{11b}-C^{11a}-C^{11} is as large as 52.4(8)° (Figure 1). When diacridine **8** was treated with MeOTf (25 equiv.) in CH_2Cl_2 in the presence of 2,6-di-*t*-butyl-4-methylpyridine (DTBMP) at room temperature, $\mathbf{2a}^{2+}(TfO^-)_2$ was obtained as an orange-yellow solid containing a small amount of DTBMP-H^+ TfO^-, which was directly treated with Zn dust in THF to give desired **1a**[11] in 49% yield over two steps (Scheme 2). In the preparation of spiroxanthene **1b**, the Tishchenko Reaction was again featured as a key step. Thus, 4',5'-dibromodispiro[xanthene-9,9'(9'*H*,10'*H*)-phenanthrene-10',9''-xanthene]

9[13] was converted to the corresponding dialdehyde **10**[14] as we reported previously, and then **10** was treated with K_2CO_3 in MeOH to give desired **1b**[11] in 33% yield (Scheme 3).



Scheme 2. Preparation of **1a** and **2a**$^{2+}$

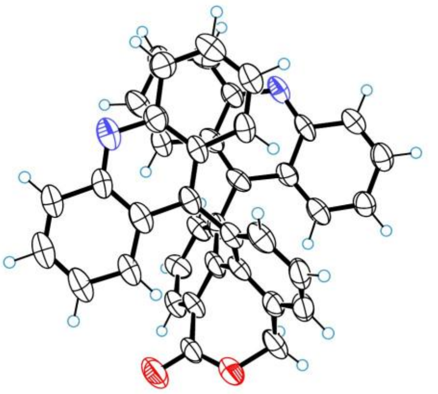
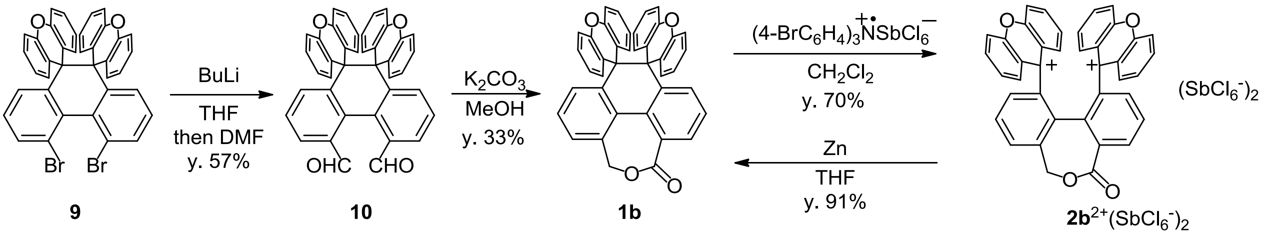


Figure 1. X-Ray structure of lactone **8**



Scheme 3. Preparation of **1b** and **2b**$^{2+}$

According to the voltammetric analyses in MeCN, **1a** undergoes 2e-oxidation at E^{ox} of +0.27 V (irrev.) vs SCE (Figure 2). Under the similar conditions, E^{ox} of **1b** is +1.08 V (irrev.), thus we can modify the electron donating ability of **1** by changing the heteroatom in the tricyclic spiro-skeletons as designed. In each case, the reduction peak appeared in the far cathodic region, which corresponds to the reduction process of bond-dissociated dication **2a**$^{2+}$(E^{red} = –0.07 V; irrev.) or **2b**$^{2+}$(+0.52 V; irrev.). Such a shift in redox peaks is characteristic to the dynamic redox pair undergoing drastic structural changes upon electron transfer.[6] Thanks to the electrochemical bistability, there would be no chance of electron-exchange between **1** and **2**$^{2+}$, which is one of the most important features in utilizing them as the memory units.

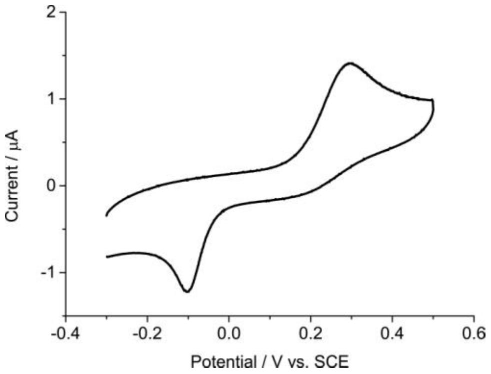


Figure 2. Cyclic voltammogram of **1a** in 0.1 M Et_4NClO_4 MeCN solution at scan rate of 100 mV s^{-1}. Pt working and counter electrodes were used.

Despite the microscopic irreversibility of electrochemical processes, the voltammograms did not change after many scans, showing that the total redox processes involving interconversion between **1** and $\mathbf{2}^{2+}$ are reversible. In fact, upon treatment of **1a** with two equiv. of one-electron oxidant $[(4\text{-}BrC_6H_4)_3N^{+\bullet}SbCl_6^-]$, $\mathbf{2a}^{2+}(SbCl_6^-)_2$[11] was isolated as a stable yellow solid in 85% yield. This is also the case of less-donating **1b**, and thus $\mathbf{2b}^{2+}(SbCl_6^-)_2$[11] was obtained in 70% isolated yield. Upon treatment with Zn dust in THF, these salts regenerated neutral donors **1a** and **1b** in respective yields of 90 and 91%. Based on the reversible interconversion, the redox pairs of **1a**,**b**/$\mathbf{2a,b}^{2+}$ can serve as novel electrochromic systems. Thus, upon constant-current electrochemical oxidation, a colorless MeCN solution of **1a** turned into yellow, and a continuous change of UV-Vis spectrum into that of $\mathbf{2a}^{2+}$ was observed (Figure 3a). Presence of several isosbestic points indicated clean conversion as well as negligible steady-state concentration of intermediary cation-radical species. The electrolysis of colorless **1b** to orange $\mathbf{2b}^{2+}$ was also followed by UV-Vis spectrum (Figure 3b). It is evident that the absorption bands of the dications $\mathbf{2}^{2+}$ differ depending on the kind of heteroatom in the cationic chromophores.

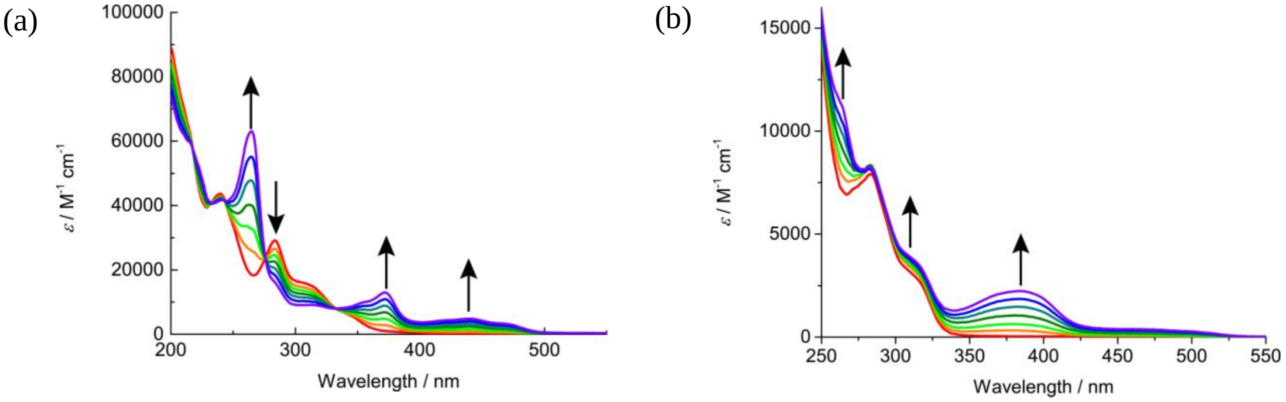


Figure 3. Changes in the UV-Vis spectra of (a) **1a** (2.54×10^{-5} M) and (b) **1b** (4.01×10^{-5} M) in MeCN (containing 0.05 M Et_4NClO_4) upon constant-current electrochemical oxidation (39 μA at 2-min interval, and 30 μA at 4-min interval, respectively). *In-situ* electrochemical reduction of the as-prepared dications $\mathbf{2a,b}^{2+}$ exhibited complete recovery of **1a**,**b**

Finally, the redox control of configurational stability was studied by VT-NMR. The methylene protons of the dihydroxepinone skeleton in spiroacridan **1a** in C_6D_6 appeared as the double doublets at 10 ºC, which gradually coalesced (T_c = 45 ºC) and became a sharp singlet at 70 ºC (Figure 4a). Based on the results, the energy barrier of the ring flip in **1a** was calculated to be 16 kcal mol^{-1}, which means easy interconversion of enantiomers at room temperature ("erasable/writable"-state). In the case of spiroxanthene **1b**, the same $\Delta G^{\ddagger}$ value (16 kcal mol^{-1} in $CDCl_3$, T_c = 40 ºC) was determined. These $\Delta G^{\ddagger}$ values are slightly larger than that for the structurally related dihydroxepin **3a** (12 kcal mol^{-1})[7] without a carbonyl group in the seven-membered ring, showing that the lactone unit slightly changes the barrier. However, more drastic changes would be observed upon oxidation of **1a**,**b**. In fact, the ^1H NMR spectra of dications **2a**,**b**$^{2+}$ showed no temperature dependence (Figure 4b), and thus the lower limit of energy barrier of **2a**$^{2+}$ was estimated as 21 kcal mol^{-1} from T_c > 150 ºC in DMSO-d_6. Thus, it is highly probable that the configuration of **2a**,**b**$^{2+}$ is stable enough for their use as "memorizing"-states.

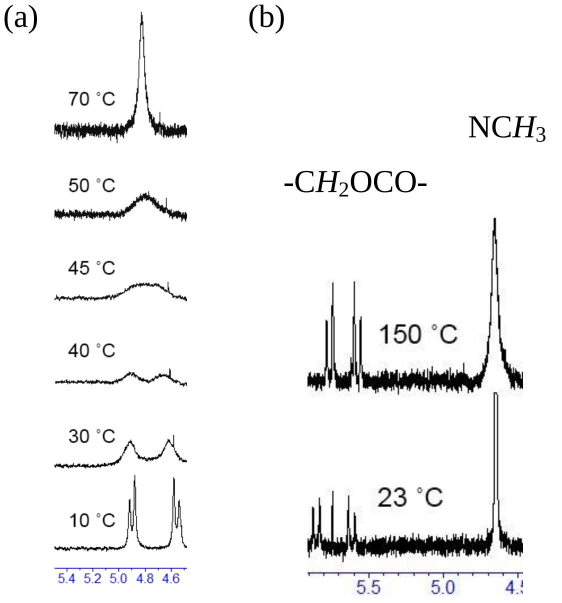


Figure 4. VT-NMR spectra of (a) spiroacridan **1a** in C_6D_6 and (b) dication **2a**$^{2+}$($SbCl_6^-$)$_2$ in DMSO-d_6

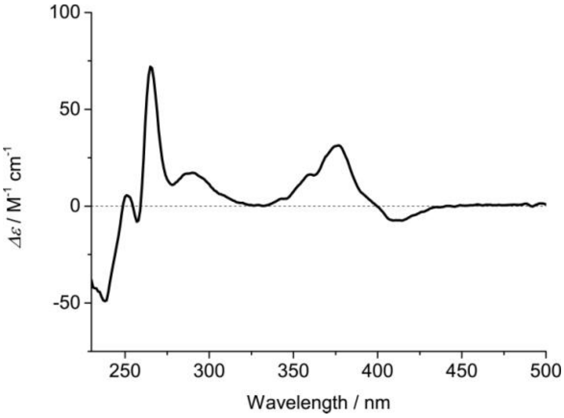


Figure 5. CD spectra of the (*M*)-**8** (1.51 x 10^{-5} M) in CH_2Cl_2.

To get more clue to the configurational stability of dications **2**$^{2+}$, optical resolution of diacridine **8** was conducted, because this precursor for the dication **2a**$^{2+}$ would have the similar energy barrier to that of **2a**$^{2+}$. Separation by using chiral HPLC (DAICEL CHIRALPAK IA) was found effective. Although the second fraction was contaminated by the antipode due to partial peak overlap, the first fraction [(*M*)-**8**] was isolated as optically pure form. The CD spectrum shown in Figure 5 did not change for a long time without any loss of CD intensity, showing that the energy barrier is quite high ($\Delta G^{\ddagger}$ > 25 kcal mol^{-1}).

In summary, we designed polycyclic lactone-based redox pairs **1a,b**/**2a,b**$^{2+}$ having spiroacridan/acridinium and spiroxanthene/xanthenylium chromophores as new entries into less well-developed category of redox-based chiral memory units. They were prepared by using the Tishchenko reaction as a key step. The electrochemical bistability characteristic to the dynamic redox systems was confirmed also in **1a,b**/**2a,b**$^{2+}$ by the large shift of redox peaks in the voltammograms. Despite microscopic irreversibility, the redox cycles between **1a,b** are **2a,b**$^{2+}$ are reversible as demonstrated by good isolated-yield interconversion as well as electrochromic behavior exhibiting isosbestic points. The drastic change in racemization barrier of **1a,b**/**2a,b**$^{2+}$ was indicated based on the VT-NMR analyses. In this way, we now conclude that the newly prepared redox pairs **1a,b**/**2a,b**$^{2+}$ are promising candidates for feature use of chiral redox memory units.

ACKNOWLEDGEMENTS

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1351.

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10. T. Seki, T. Nakajo, and M. Onaka, *Chem. Lett.*, 2006, **35**, 824; Typical procedure: A suspension of dialdehyde **7** (150 mg, 266 μmol) and K_2CO_3 (220 mg, 1.59 mmol) in MeOH 6 mL was stirred at 27 ˚C for 15.5 h. After diluted with water, the whole mixture was extracted with $CHCl_3$. The combined organic layers were washed with water and brine, and dried over anhydrous Na_2SO_4. After filtration, the crude reaction mixture was concentrated under reduced pressure. The residue was purified by recrystallization from EtOH to give lactone **8** (64.7 mg) as a yellow solid. Mother liquor was purified by flash chlomatography on silica gel ($CHCl_3$: EtOAc = 1 : 1, 0.5% v/v Et_3N) to give **8** (40.3 mg) as a yellow solid in a total yield of 70%.
11. Data for **1a**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.90 (1H, dd, 1.8 Hz, 7.1 Hz) 7.44 (1H, dd, *J* =1.8 Hz, 6.6 Hz), 7.19-7.35 (4H, m), 6.99 (4H, ddd, *J* = 1.8 Hz, 8.3 Hz, 8.3 Hz), 6.79 (1 H, d, *J* = 7.9 Hz), 6.38-6.64 (7H, m), 6.20 (2H, br-s), 5.77 (1H, d, 7.3 Hz), 5.71 (1H, d, *J* = 7.2 Hz), 5.39 (1H, d, *J* = 12.5 Hz), 5.22 (1H, d, *J* = 12.5 Hz), 2.73 (3H, s), 2.72 (3H, s); IR (KBr) ν cm^{-1} 3069, 2961, 2871, 2820, 1720, 1591, 1475, 1427,1383, 1363, 1324, 1280, 1245, 1169, 1135, 1101, 1059, 1039, 896, 863, 793, 750, 699, 657; LR-MS (EI) *m/z* 594 (M^+, BP), 579 ($[M-CH_3]^+$, 98), 535 ($[M-CH_3-CO_2]^+$, 9.7), 446 (11), 368 (12), 297 (M^{2+}, 21), 278 (74), 185 (13), 171 (11), 157 (16), 129 (29), 97 (24), 83 (28), 57 (51).

    Data for **1b**: ^{1}H NMR (300 MHz, $CDCl_3$) δ7.99 (1H, ddd, *J* = 1.8 Hz, 4.4 Hz, 9.0 Hz), 7.54 (1H, td, *J* = 1.4 Hz, 7.2 Hz), 7.33-7.37 (3H, m), 7.22-7.28 (2H, m), 7.19 (2H, br-s), 7.04 (2H, br-s), 6.82 (2H, br-s), 6.71 (1H, br-s), 6.61 (4H, br-s), 6.46 (2H, br-s), 5.72 (2H, br-s), 5.42 (1H, br-d, *J* = 9.5 Hz), 5.27 (1H, br-d, *J* = 9.5 Hz); IR (KBr) ν cm^{-1} 3066, 2923, 2855, 1713, 1598, 1571, 1477, 1442, 1374, 1309, 1281, 1241, 1132, 1100, 1038, 900, 867, 775, 751, 707, 651; LR-MS (EI) *m*/*z* = 568 (M^+, bp).

Data for $\mathbf{2a}^{2+}(\mathrm{SbCl}_6^-)_2$: ^{1}H NMR (300 Hz, CD_3CN) δ 8.46 (2H, dd, *J* = 7.9 Hz, 8.8 Hz) 8.29 (1H, dd, *J* = 1.5 Hz, 6.4 Hz, 9.3 Hz), 8.26 (1H, dd, *J* = 1.5 Hz, 6.8 Hz), 8.07-8.14 (1H, m), 8.08 (2H, dd, *J* = 1.5 Hz, 7.9 Hz), 8.02 (1H, br-d, *J* = 8.8 Hz), 8.00 (2H, dd, *J* = 1.1 Hz, 7.9 Hz), 7.63-7.72 (1H, m), 7.68 (2H, dd, *J* = 7.9 Hz, 7.9 Hz), 7.59 (2H, dd, *J* = 7.9 Hz, 7.9 Hz), 7.54 (1H, dd, *J* = 1.1 Hz, 8.6 Hz), 7.32 (1H, ddd, *J* = 1.1 Hz, 6.4 Hz, 8.8 Hz), 7.27 (1H, ddd, *J* = 1.1 Hz, 6.4 Hz, 8.6 Hz), 7.13 (1H, dd, *J* = 1.5 Hz, 7.9 Hz), 7.06 (1H, dd, *J* = 1.5 Hz, 7.9 Hz), 6.41 (1H, dd, *J* = 1.1 Hz, 8.6 Hz), 6.29 (1H, br-d, *J* = 8.8 Hz), 5.66 (1H, d, *J* = 12.6 Hz), 5.50 (1H, d, *J* = 12.6 Hz), 4.54 (3H, s), 4.52 (3H, s). IR (KBr) ν cm^{-1} 3083, 2957, 1727, 1608, 1578, 1548, 1460, 1445, 1370, 1278, 1192, 1099, 1026, 1015, 765, 707, 653, 602.

Data for $\mathbf{2b}^{2+}(\mathrm{SbCl}_6^-)_2$: ^{1}H NMR (300 MHz, CD_3CN) δ 8.54 (1H, d, *J* = 7.2 Hz), 8.49 (1H, d, *J* = 7.2 Hz), 8.36 (2H, dd, *J* = 3.9 Hz, 7.8 Hz), 8.27 (1H, d, *J* = 3.9 Hz), 8.23 (2H, dd, *J* = 2.4 Hz, 6.6 Hz), 8.14 (1H, d, *J* = 7.5 Hz), 7.79-7.87 (4H, m), 7.70-7.77 (2H, m), 7.54-7.64 (4H, m), 7.29 (1H, d, *J* = 7.9 Hz), 7.23 (1H, d, *J* = 7.9 Hz), 6.80 (1H, d, *J* = 8.6 Hz), 6.70 (1H, d, *J* = 8.6 Hz), 5.74 (1H, d, *J* = 12.8 Hz), 5.57 (1H, d, *J* = 12.8 Hz); IR (KBr) ν cm^{-1} 3075, 2954, 2925, 2855, 1728, 1621, 1598, 1577, 1537, 1502, 1367, 751.

Data for **8**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.08 (1H, d, *J* = 8.8 Hz), 8.03 (1H, d, *J* = 8.8 Hz), 7.95 (1H, dd, *J* = 1.5 Hz, 7.9 Hz), 7.69 (1H, dd, *J* = 1.3 Hz, 7.9 Hz), 7.61 (2H, br-d, *J* = 7.9 Hz), 7.57 (1H, br-d, *J* = 6.0 Hz), 7.41 (2H, dd, *J* = 7.9 Hz, 7.9 Hz), 7.40 (1H, dd, *J* = 1.1 Hz, 7.9 Hz), 7.29-7.37 (3H, m), 7.23 (2H, d, *J* = 10.3 Hz), 7.14 (1H, ddd, *J* = 0.9 Hz, 6.4 Hz, 8.8 Hz), 7.03 (1H, dd, *J* = 1.5 Hz, 7.9 Hz), 6.98 (1H, dd, *J* = 1.3 Hz, 7.9 Hz), 6.70-6.77 (2H, m), 5.79 (1H, d, *J* = 8.8 Hz), 5.68 (1H, d, *J* = 8.4 Hz), 5.57 (1H, d, *J* = 11.7 Hz), 5.36 (1H, d, *J* = 11.7 Hz); IR (KBr) ν cm^{-1} 3063, 1728, 1626, 1608, 1554, 1538, 1517, 1460, 1436, 1407, 1370, 1353, 1263, 1227, 1083, 1013, 856, 818, 795, 751, 690, 649, 639, 629, 618, 612, 603 cm^{-1}; LR-MS (FD) *m*/*z* 564 (M^+, BP).

12. Crystal data of **8**•$CHCl_3$: $C_{41}H_{25}N_2O_2Cl_3$, *M* 564.63, triclinic *P*-1, a = 9.506(10) Å, b = 12.48(2) Å, c = 14.54 (2) Å, α = 109.84(2) °, β = 93.32 (2) °, γ = 98.47(2) °, V = 1594.1(2) Å^3, Z = 2, D_c = 1.42 gcm^{-3}, independent reflection 6844 (all), 4304 (2σ), T = 153 K, R = 9.7%, CCDC 951650.
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