

Preparation and Magnetic Properties of Radical Anion Salts Derived from Styrylpyryliums and the Corresponding Photo-Dimers[#]

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The preparation and magnetic properties of organic radical anion salts derived from styrylpyrylium derivatives **1a** and **2a** are described and compared to those of the corresponding photo-dimers. The magnetic properties of the radical anions for TCNQ salt **1b** and TCNQF₄ salt **1c** are rather different, showing antiferromagnetic interactions based on the 1-D Heisenberg model in the former, and ferromagnetic interactions in the latter. This difference is considered to be a result of the fairly large difference in their crystal structures. A considerable change in the magnetic properties was found between the radical anion salts of monomers and the corresponding photo-dimers, in which magnetic susceptibilities are largely diminished.

The search for novel spin systems with multiple properties is of current interest in the field of molecular-based magnetic materials to examine the synergy between magnetic properties and other properties such as conduction, optical, liquid crystalline, and other physical properties.¹ As for the development of organic spin systems with optical properties, several groups have recently developed intriguing organic photo-responsive spin systems. Iwamura, Matsuda et al. reported in 1998 an azobenzene derivative carrying two nitronyl nitroxide radicals, and observed its UV as well as its EPR spectral change upon irradiation in solution.² Matsuda, Irie et al. have succeeded in switching the intramolecular spin-spin interactions efficiently in their elaborate diarylethene systems.³ Veciana and his collaborators have reported on interesting photo-dimerization in an iminoferrocene derivative with a triphenylmethyl radical.⁴ In this case, although no reverse reaction was reported, photo-induced intramolecular isomerization and the successive dimerization were observed to give this diradical. Interesting examples of 2-D photochromic molecular based magnets, such as (spiropyran)MCr(ox)₃, that show a change in their hysteresis loops upon irradiation have also been reported recently by

Pei Yu et al.⁵

In the course of our studies in the development of organic multifunctional spin systems,⁶ including heat-responsive systems,⁷ we have also been interested in developing spin systems with photo-responsive properties to observe the alteration of intermolecular spin-spin interactions based on the structural change. We have hitherto reported norbornadiene derivatives,⁸ spiropyran derivatives⁸ and anthracene derivatives⁹ with TEMPO (2,2,6,6-tetramethyl-1-piperidinyloxy) substituents as spin sources. In the studies on the anthracene and the corresponding dimer systems with TEMPO substituents, we dealt with *intermolecular* photo-dimerization reactions, and found that the signs and the magnitudes of intermolecular magnetic interactions could be changed, in principle, by outer stimuli such as light, heat, or appropriate solvents in a reversible system derived from 9-methylantracene with 4-amino-TEMPO.⁹ Since that time, except the anthracene and the corresponding dimer systems, only one example of an iminoferrocene derivative with triphenylmethyl radical⁴ has been found in which *intermolecular* photo-dimerization reaction was used to change the magnetic properties. We then have

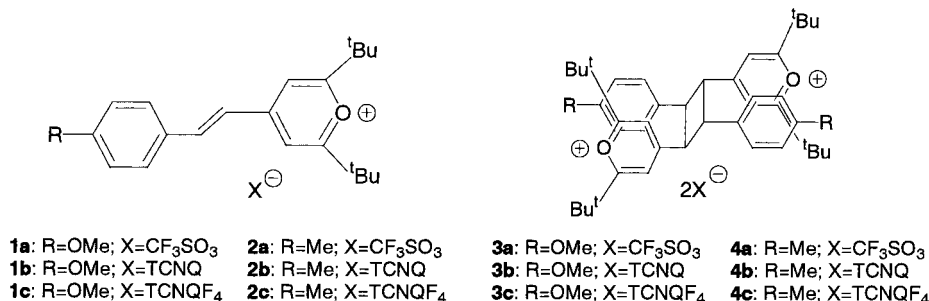
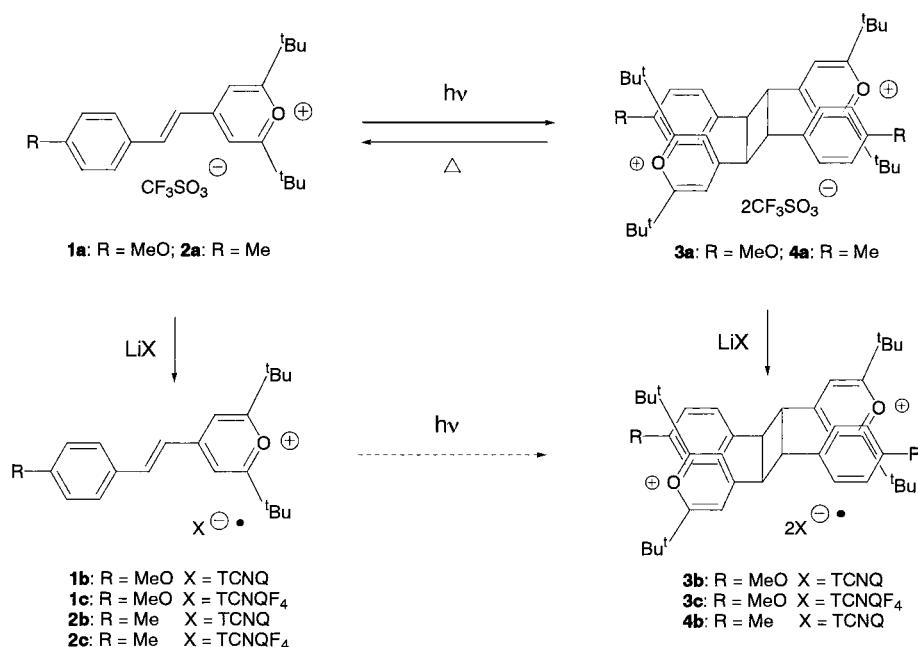


Chart 1.

[#] This paper is dedicated to Emeritus Professor Soichi Misumi on the occasion of his 77th birthday.



Scheme 1.

sought other possible candidates. It was reported that some styrylpyrylium salts give the corresponding photo-dimers in an *intermolecular* manner which, in turn, dissociate by heating in solution to the starting salts.¹⁰ We have been interested in introducing a spin center to this attractive reversible system. Moreover, the photo-dimerization of a methanesulfonate salt of *p*-methoxy **1a** to the corresponding dimer **3a** (Chart 1) is known to be a typical example of a single-crystal-to-single-crystal reaction.¹¹ In this paper, we wish to report on the preparation, the structures, and the magnetic properties of some styrylpyrylium derivatives, and the corresponding photo-dimers with radical anions from TCNQ or TCNQF₄ as spin sources.¹²

Results and Discussion

Preparation of Radical Anion Salts of Styrylpyrylium and the Corresponding Dimers. The trifluoromethanesulfonate salts of styrylpyrylium derivatives (R = *p*-MeO: **1a** and R = *p*-Me: **2a**) were prepared by the condensation of 2,6-di-*t*-butyl-4-methylpyrylium trifluoromethanesulfonate with *p*-anisaldehyde or *p*-tolualdehyde in acetic acid according to the method described by Hesse and Hünig.¹¹ The anion exchange of the trifluoromethanesulfonate salts was carried out by using LiTCNQ or LiTCNQF₄ in a mixed solvent of acetonitrile and water to give the corresponding radical anion salts (**1b**, **1c**, **2b**, and **2c**) in moderate yields (Scheme 1).

We then tried to prepare photo-dimers of the styrylpyrylium radical anion salts by irradiation under various conditions in solution or in the solid-state. Unfortunately, however, no fruitful result was obtained for the direct photo-dimerization reaction by the irradiation of each radical anion salt with a mercury lamp or other light sources such as a Xe lamp. Instead, the corresponding radical anion salts of photo-dimers could be obtained by indirectly way. So, at first, the trifluoromethanesulfonate salts of the dimers (**3a**, **4a**) were prepared by irradiation of the corresponding salts of monomers and then the an-

ions of the dimers were exchanged with LiTCNQ or LiTCNQF₄ to give the desired radical anion salts of the dimers (**3b**, **3c**, **4b**, and **4c**).

Magnetic Properties of Radical Anion Salts of Styrylpyrylium Derivatives and X-ray Analysis of 1b. The magnetic susceptibility of each radical anion salt was measured by a SQUID susceptometer in the temperature region 2 K to 300 K. The temperature dependence data of χT -values for the TCNQ radical anion salt of *p*-methoxy derivative (**1b**) is shown in Fig. 1 (left), from which the existence of antiferromagnetic interactions is apparent. It has also been found from the data of the χ -values shown in Fig. 1 (right) that the behavior can be well expressed using the one dimensional (1-D) antiferromagnetic Heisenberg model¹³ with a J -value of -5.42 K. In addition, the spins of TCNQ radical anions have been found to remain unchanged without any appreciable decrease in the χ -values. The magnetic behavior is rather similar to that of the radical anion salts of cyanine derivatives reported by Takagi et al.,¹⁴ which provides another example of a typical $S = 1/2$ Heisenberg antiferromagnetic (AFM) chain, although the J -value is smaller in the present system.

The molecular structures of each component in **1b** obtained by X-ray analysis are shown in Fig. 2 (left) and its crystal structure in Fig. 2 (right), respectively. It was apparent from the analysis that the styrylpyrylium as well as TCNQ molecules have relatively high planarity in the salt and that they are stacked along the *b*-axis to form alternate columns. This packing feature is quite different from that of the trifluoromethanesulfonate salt of the same styrylpyrylium derivative, in which the styrylpyrylium molecules are stacked almost in a segregate manner.¹² Since the salt has the space group $P2_1/m$, the distance between a styrylpyrylium and a TCNQ molecule is estimated to be 3.43 Å, and that of a couple of TCNQ molecules to be 6.87 Å. The 1-D Heisenberg AFM behavior found in the salt is considered to be based on the interactions between the spins in the TCNQ radical anions along

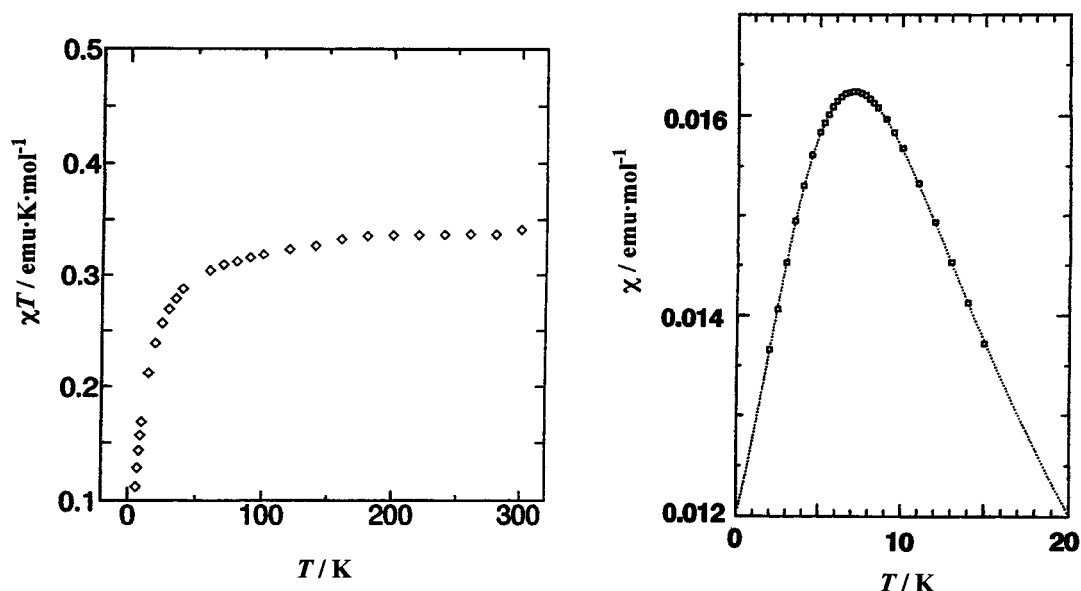


Fig. 1. (Left) Temperature dependence of χT values for **1b**. (Right) Temperature dependence of χ values for **1b**. The calculated data are indicated as the solid line.

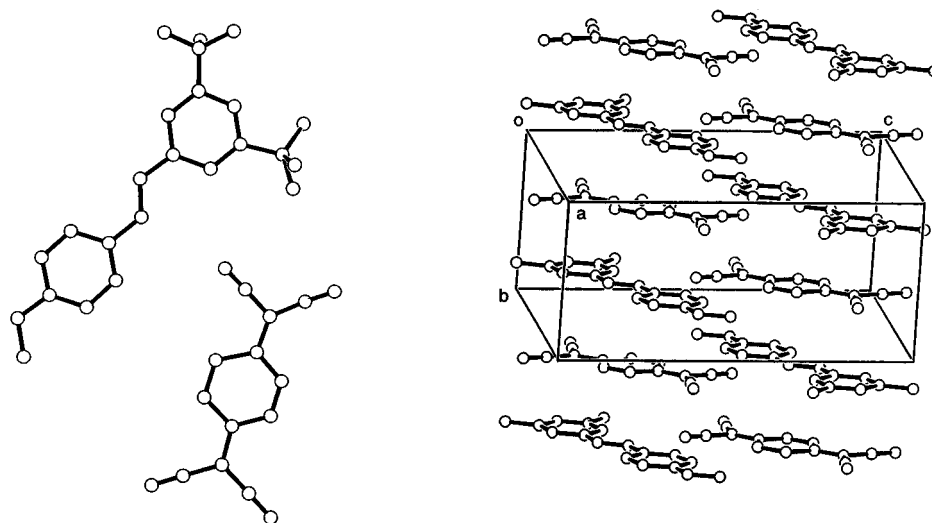


Fig. 2. (Left) Molecular structures of the pyrylium cation and TCNQ in **1b**. (Right) Crystal structure of **1b** viewed almost along the *a*-axis. The hydrogen atoms and the methyl groups in *t*-butyl groups are omitted for clarity because of occurrence of the disorder by the rotation of the methyl groups in the latter case.

the stacking direction through the intercalated styrylpyrylium molecules, as significant intercolumnar interactions would be almost impossible in the present case. Owing to the remote spin centers, the J -value (-5.4 K) observed in the salt is smaller than that of the radical anion salt MEM-(TCNQ)₂, which is reported to be a typical one-dimensional $S = 1/2$ Heisenberg antiferromagnet with $J/k_B = -53$ K.¹⁵ From the point of view of photochemical dimerization, the alternated stacking feature of the salt is considered to be unsuitable for the reaction in the solid-state, and, as the consequence, the photochemical dimerization was unsuccessful not only in the solid-state but also in solution.

Magnetic Properties of Radical Anion Salts of Styrylpyrylium Derivatives and X-ray Analysis of **1c.** The magnetic behavior of the TCNQF₄ radical salt of the *p*-methoxy deriva-

tive (**1c**) is rather different from the TCNQ salt, as shown in Fig. 3 (left). Ferromagnetic interactions (FM) are apparent in the lower temperature range and the behavior is well expressed by the 1-D ferromagnetic Heisenberg model with small interactions ($J = +0.65$ K) (Fig. 3, right). Thus, distinct changes in the magnetic behavior have been found in the styrylpyrylium salts by changing counter radical anions.

The molecular structures of the salt **1c** and its crystal structure obtained by X-ray analysis are shown in Fig. 4 (left). The alternate stacking feature observed in the previous salt **1b** has also been found in the TCNQF₄ salt **1c**. The styrylpyrylium and TCNQF₄ molecules are stacked along the *c*-axis with two types of intermolecular distances (3.35 Å and 3.38 Å) between the styrylpyrylium and TCNQF₄ molecules. Short contacts of ca. 3.5 Å are also found between the F and N atoms in

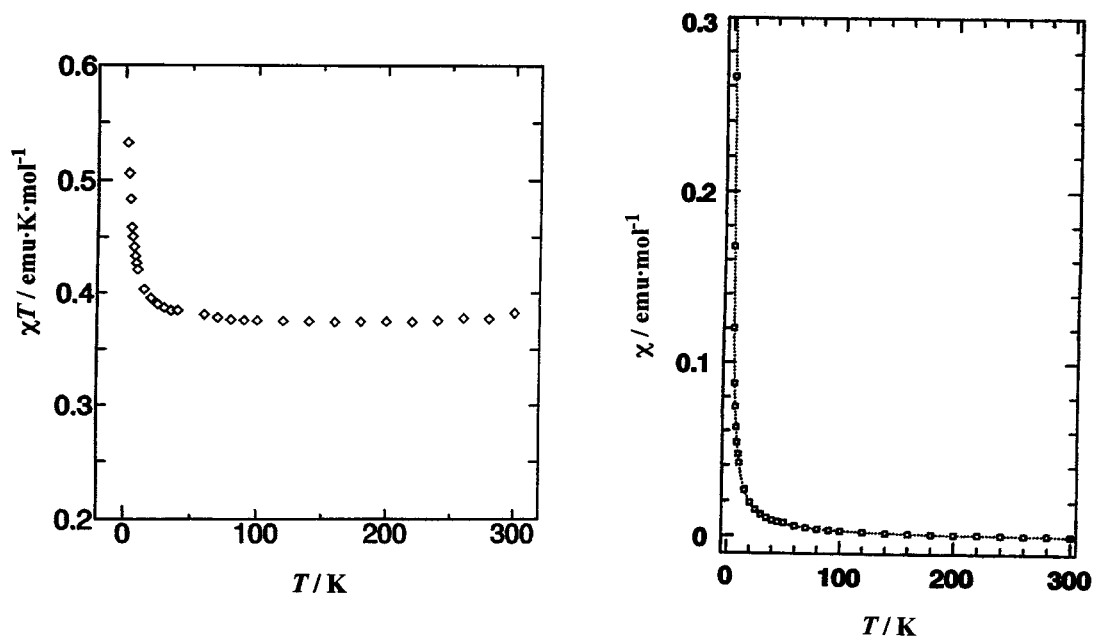


Fig. 3. (Left) Temperature dependence of χT values for **1c**. (Right) Temperature dependence of χ values for **1c**. The calculated data are indicated as the solid line.

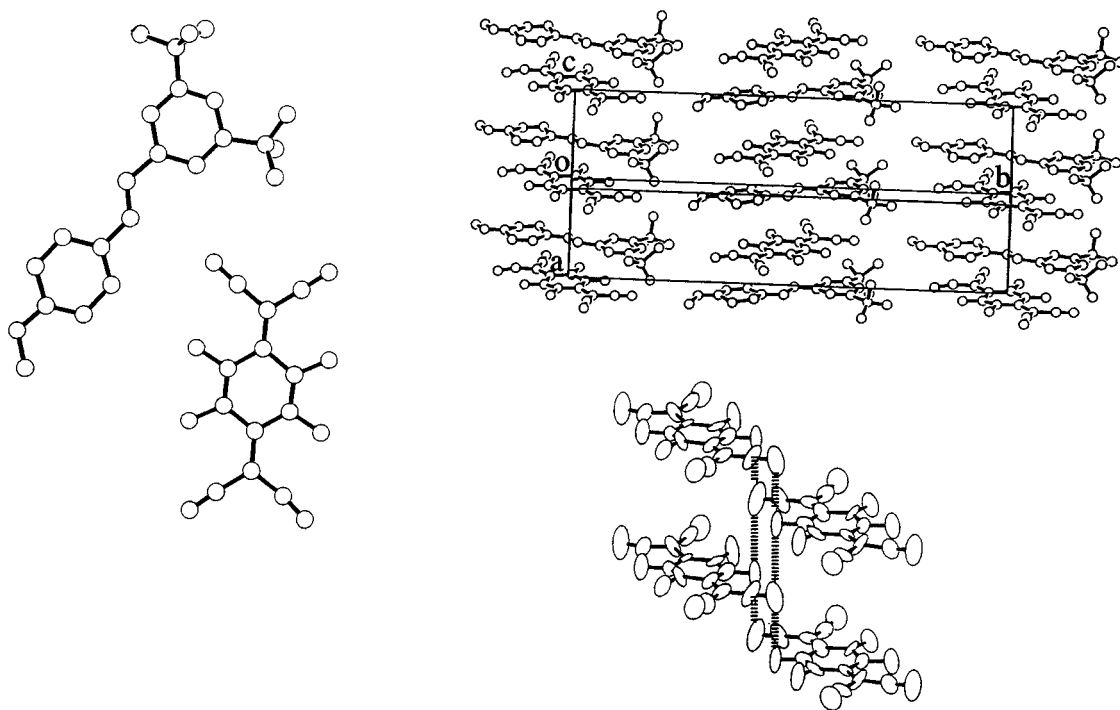


Fig. 4. (Left) Molecular structures of the pyrylium cation and TCNQ in **1c**. (Right, upper) Crystal structure of **1c** viewed along the *a*-axis. The hydrogen atoms are omitted for clarity. (Right, lower) Selected TCNQF₄ molecules of **1c** with indication of the interactions between fluorine and nitrogen atoms (broken lines).

the TCNQF₄ molecules, as shown in Fig. 4 (right/lower), which are supposed to be relevant to the observed 1-D ferromagnetic interactions in this radical anion salt. When the spin polarization effect is taken into account through the short contacts between F and N atoms, the spin-spin interactions between the nearest TCNQF₄ radical anions in the neighboring columns are antiferromagnetic, while those between the

TCNQF₄ radical anions in the stacked direction are ferromagnetic. Therefore, the occurrence of 1-D ferromagnetic interactions is thought to be possible in this case. Thus, the difference in the magnetic properties found in **1b** and **1c** can be derived from the apparent difference in their crystal structures.

On the other hand, similar magnetic behavior has been found in TCNQ and TCNQF₄ radical anion salts of *p*-methyl

Table 1. Magnetic Data of Radical Anion Salts of Monomers^{a)}

Salts	<i>J</i> -value/K	Magnetic Interaction
1b	−5.42	antiferromagnetic
1c	0.64	ferromagnetic
2b	−2.95	antiferromagnetic
2c	−2.80	antiferromagnetic

a) Fitting for 1-D Heisenberg model.

Table 2. Magnetic Data of Radical Anion Salts of Dimers^{a)}

Salts	Curie constant/ emu K mol ^{−1}	Weiss temperature/K	Magnetic Interaction
3b	0.058	−0.83	antiferromagnetic
3c	0.072	−0.11	antiferromagnetic
4b	0.058	−0.15	antiferromagnetic

a) Fitting for Curie-Weiss law.

derivatives (**2b**, **2c**) that are well expressed by 1-D Heisenberg AFM interactions with small *J*-values, as shown in Table 1 together with those of **1b**, **1c**.

Magnetic Properties of Radical Anion Salts of Dimers. From the magnetic data of the radical anion salts of dimers **3b**, **3c**, and **4b** shown in Table 2, it is apparent that the Curie constants of the radical anions of the dimers decrease greatly compared with those of the salts of monomers, presumably because of the singlet formation between the radical anions irrespective of the sort of radical anions. It is thus obvious that the magnetic properties of a radical anion salt can be significantly changed, in principle, by photo-dimerization, and the distinct difference in magnetic behaviors found in each monomer/dimer pair provides a potential switching system of magnetic properties by external photo stimuli. However, the monomer/dimer pairs of the radical anions could not be directly exchanged photochemically in this case, indicating the limitations of the usage of TCNQ or TCNQF₄ radical anion salts for this photochemical reaction.¹⁶

Conclusion

A couple of styrylpyrylium derivatives (**1a**, **2a**) were prepared as trifluoromethanesulfonate salts, from which TCNQ and TCNQF₄ salts (**1b**, **1c**, **2b**, **2c**) were derived by anion exchange reactions. The magnetic properties of the radical anions for **1b** and **1c** are rather different, showing antiferromagnetic interactions based on the 1-D Heisenberg model in the former, and ferromagnetic interactions in the latter. This, and the fairly large difference in their crystal structures is considered to be responsible for the difference in the magnetic properties. Although the direct photo-dimerization of the monomers was unsuccessful, the corresponding radical anion salts of the dimers were obtained in an indirect way through the anion exchange from the triflates of the photo-dimers. The radical anion salts of dimers show largely diminished magnetic susceptibilities, presumably because of the singlet formation between the radical centers. Thus, although the monomer/dimer pairs of radicals anions could not be directly exchangeable, distinct differences in the magnetic behavior found in each pair provides some potentially attractive examples of photo-responsive spin systems.

Experimental

Materials. LiTCNQ and LiTCNQF₄ were prepared from LiI and TCNQ or TCNQF₄. *p*-Methoxystyrylpyrylium trifluoromethane sulfonate **1a** and *p*-methylstyrylpyrylium trifluoromethane sulfonate **2a** were prepared as described by Hesse and Hünig.¹¹

Instrumentation. Melting points were measured on a YAMATO MP-21 apparatus and are uncorrected. MS data was taken using a JEOL JMS-AX 505 mass spectrometer. EPR spectra were obtained on a JEOL JES-FE3XG spectrometer and each *g*-value was determined using a Mn²⁺/MgO maker as an internal standard. Magnetic susceptibility measurements were carried out on a QUNTUM DESIGN MPMS-5 SQUID susceptometer using ca. 10 mg for each powdered sample, correcting diamagnetic contributions in the usual way.¹⁷

X-ray Structure Determination. X-ray diffraction data were collected at room temperature on a Rigaku RAXIS4 diffractometer with Mo-K α radiation for **1b** and on a Bruker AXS SMART 1000 diffractometer with Mo-K α radiation for **1c**, respectively. The structures were solved by direct methods and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. All calculations were performed using the teXsan (Molecular Structure Corporation) and the crystals (Chemical Crystallography Laboratory, Oxford University) crystallographic software packages.

Preparation of Radical Anion Salts of Styrylpyrylium Derivatives. A typical procedure is exemplified for **1b** and is as follows; To a stirred solution of **1a** (56 mg, 0.12 mmol) in a solvent (10 mL) of acetonitrile and water (1:1) was added LiTCNQ (25 mg, 0.12 mmol) in a mixed solvent as above at ambient temperature. A dark solid precipitated immediately and was collected by the filtration under reduced pressure and then recrystallized from acetonitrile to give **1b** as black needles (39 mg, 60%), mp 209–211 °C. Found: C, 77.11; H, 6.42; N, 9.86%. Calcd for C₃₄H₃₃N₄O₂: C, 77.10; H, 6.28; N, 10.58%. EPR (acetone): 1 line, *g* = 2.010. In a similar manner, other radical anion salts (**1c**, **2b**, **2c**) were prepared and the data are as follows;

1c: black needles, mp 248–251 °C. Found: C, 68.03; H, 4.93; N, 9.40%. Calcd for C₃₄H₂₉F₄N₄O₂: C, 67.88; H, 4.86; N, 9.31%. EPR (acetone): 1 line, *g* = 2.010.

2b: black needles, mp 210–211 °C. Found: C, 79.90; H, 6.38; N, 10.66%. Calcd for C₃₄H₃₃N₄O: C, 79.50; H, 6.48; N, 10.91%. EPR (acetone): 1 line, *g* = 2.011.

2c: black needles, mp 241–243 °C. Found: C, 69.97; H, 5.03; N, 9.59%. Calcd for C₃₄H₂₉F₄N₄O: C, 69.73; H, 4.99; N, 9.57%. EPR (acetone): 1 line, *g* = 2.011.

Preparation of Radical Anion Salts of Dimers. In a vessel (200 mL) for photochemical reactions with a pyrex filter was placed an acetic acid solution (15 mL) of **1a** (2.3 g, 4.9 mmol) and irradiated with high-pressure Hg-lamp (400 W) under nitrogen at ambient temperature. The resulting precipitates was filtered and then dried to give dimer **3a**¹¹ (1.8 g, 78%). The dimer thus obtained was dissolved in a solvent (10 mL) of acetonitrile and water (1:1) and then LiTCNQ (66 mg, 0.32 mmol) in a mixed solvent as above was added at ambient temperature. A dark green solid formed immediately and was collected by the filtration under reduced pressure to give **3b** as a dark green powder (0.15 g, 86%), mp 96–99 °C. Found: C, 76.77; H, 6.44; N, 9.40%. Calcd for C₆₈H₆₆N₈O₄: C, 77.10; H, 6.28; N, 10.58%. EPR (acetone): 1 line, *g* = 2.011. In a similar manner, other radical anion salts (**3c**, **4b**, **4c**) were prepared and the data are as follows;

3c: black needles, mp 138–140 °C. Found: C, 68.03; H, 4.93; N, 9.40%. Calcd for $C_{68}H_{58}F_8N_8O_4$: C, 67.88; H, 4.86; N, 9.31%. EPR (acetone): 1 line, $g = 2.011$.

4b: dark green powders, mp 110–112 °C. Found: C, 79.90; H, 6.38; N, 10.66%. Calcd for $C_{68}H_{66}N_8O_2$: C, 79.50; H, 6.48; N, 10.91%. EPR (acetone): 1 line, $g = 2.011$.

4c: dark green powders, mp 123–124 °C. Found: C, 69.62; H, 5.12; N, 9.94%. Calcd for $C_{68}H_{58}F_8N_8O_2$: C, 69.73; H, 4.99; N, 9.57%. EPR (acetone): 1 line, $g = 2.011$.

Crystal Structure Determination of Compounds 1b and 1c. Among the radical anions prepared, single crystals suitable for X-ray diffraction were obtained for **1b** and **1c** and their crystal data are as follows;

Crystal Data for 1b: $C_{34}H_{33}N_4O_2$, $M_r = 529.66$, monoclinic, $a = 14.257(8)$ Å, $b = 6.8727(7)$ Å, $c = 15.853(4)$ Å, $\beta = 97.95(4)^\circ$, $V = 1538.4(8)$ Å³, $T = 295$ K, space group $P2_1/m$, $Z = 2$, $D_c = 1.143$ g cm⁻³. $R = 0.099$, $wR = 0.097$ [2560 observed reflections and 245 parameters, $I > 3\sigma(I)$].

Crystal Data for 1c: $C_{34}H_{29}N_4O_2F_4$, $M_r = 601.62$, orthorhombic, $a = 16.494(2)$ Å, $b = 28.275(4)$ Å, $c = 6.7405(9)$ Å, $V = 3143(1)$ Å³, $T = 295$ K, space group $Pna2_1$, $Z = 4$, $D_c = 1.271$ g cm⁻³. $R = 0.063$, $wR = 0.038$ [767 observed reflections and 396 parameters, $I > 2\sigma(I)$].

The X-ray crystallographic data (bond lengths and angles, atomic coordinates, and anisotropic thermal parameters) for **1b** and **1c** are deposited at the Editorial Office which will be available upon request.

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