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Control in spin-delocalization into the 2-substituted π-systems in 3-oxophenalenoxyl neutral radicals: evaluation by their dimeric structures and DFT calculations

Shinsuke Nishida,[a,b,†] Yasushi Morita,[a,c,*] Tomohiro Ohba,[a] Kozo Fukui,[c] Kazunobu Sato,[b] Takeji Takui[b,*] and Kazuhiro Nakasuji[a,*]

[a] *Department of Chemistry, Graduate School of Science, Osaka University, Toyonaka, Osaka 560-0043, Japan*
[b] *Department of Chemistry, Graduate School of Science, Osaka City University, Sumiyoshi-ku, Osaka 558-8585, Japan*
[c] *PRESTO, Japan Science and Technology Agency, Honcho Kawaguchi, Saitama 332-0012, Japan*

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Abstract—3-Oxophenalenoxyl derivatives, neutral π-radicals having two oxygen atoms at 1,3-position on a phenalenyl skeleton, possess most of their spin densities at the two oxygen atoms and the 2-position, featuring in easy dimerization at the 2-position. For the decrease in spin density at the 2-position by invoking spin-delocalization into the 2-substituted π-systems, we have designed 2-thienyl-3-hydroxyphenalenone derivatives as synthetic precursors of neutral π-radicals, and conducted their oxidation reactions by using a variety of oxidants. The chemical structures of the dimer obtained were unambiguously determined by FABMS, IR, and NMR spectra with help of density functional theory calculations, showing the formation of the bonds on the thienyl moieties. These observations and DFT calculations illustrate the occurrence of a considerable amount of spin-delocalization into the 2-substituted-thienyl moieties from the 3-oxophenalenoxyl skeletons.

1. Introduction

Stable organic π-radicals have attracted much attention for both molecule-based magnetic materials[1] and single-component organic conductors.[2] In order to synthesize new stable organic π-radicals as components of these molecule-based functionality materials, we have extensively studied phenalenyl-based π-radicals with spin-delocalized and highly spin-polarized nature. Some of these π-radicals are extremely stable in air, and exhibit intriguing magnetic and optical propeties.[3] Oxophenalenoxyl systems are a new class of neutral π-radicals possessing two oxygen atoms on a phenalenyl skeleton as substituents. Among these systems, 6- and 4-oxophenalenoxyls **1**[4] and **2**[5a] have high stability in air due to extensively spin-delocalized nature on the phenalenyl π-systems. These two π-radicals are topological isomers, exhibiting the unique spin density distribution nature depending on the connectivity of the two oxygen atoms on the phenalenyl skeleton, coined as topological symmetry control in spin density distribution.[5] In contrast, a 3-oxophenalenoxyl derivative **3** with methoxyphenyl moiety at the 2-position, a topological isomer of **1** and **2**, easily gave dimeric compound **4** having a C–C bond between the 2- and 2′-positions.[6] This indicates that the spin density of **3** dominates at the 2-position, although a appreciable amount is delocalized into the methoxyphenyl moiety. In order to decrease the spin density at the 2-position by invoking spin-delocalization into the 2-substituted π-systems, we have designed 2-thienyl-substituted 3-oxophenalenoxyl derivatives **5a** and **5b**. Thiophene, a well-known five-membered ring system, is likely to have a co-planar structure with the 3-oxophenalenoxyl skeleton, which is favorable for an extension of π-conjugated systems. Oxidation of 3-hydroxyphenalenone derivatives **6a**[7] and **6b** has given dimeric compounds **7** and **8**. Interestingly, their dimeric structures feature in the formation of the bonds at the carbon atoms of their thienyl moieties. In this study, we have elucidated electronic-spin structures of **5a** and **5b** in terms of the dimeric structures of **7** and **8** determined by spectroscopic studies and density functional theory (DFT) calculations from the theoretical side. These results illustrate that considerable amounts of spin densities are delocalized into the 2-substituted-thienyl moieties in the neutral π-radicals **5a** and **5b**.

Keywords: 3-Oxophenalenoxyl; Neutral radical; Dimeric compounds; Spin density.

* Corresponding authors. Tel.: +81 6 6850 5393; fax: +81 6 6850 5395; e-mail: morita@chem.sci.osaka-u.ac.jp

[†] Japan Society for the Promotion of Science fellow PD.

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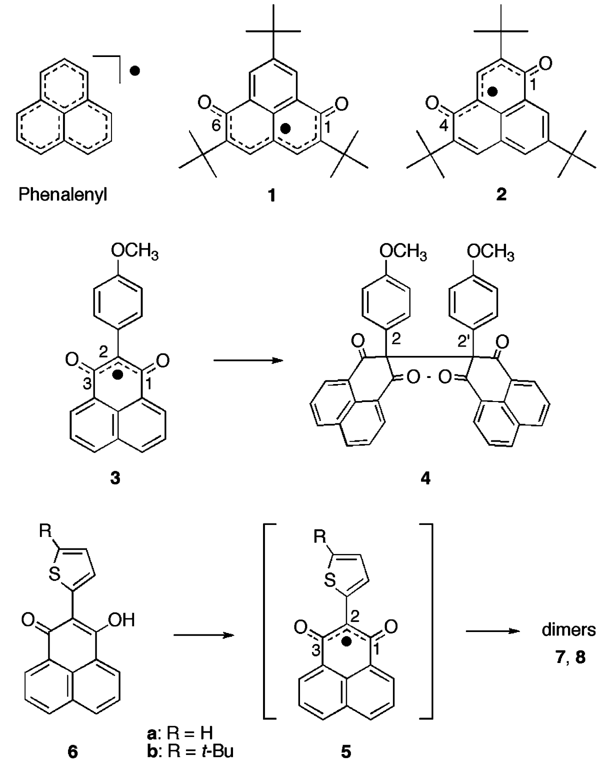
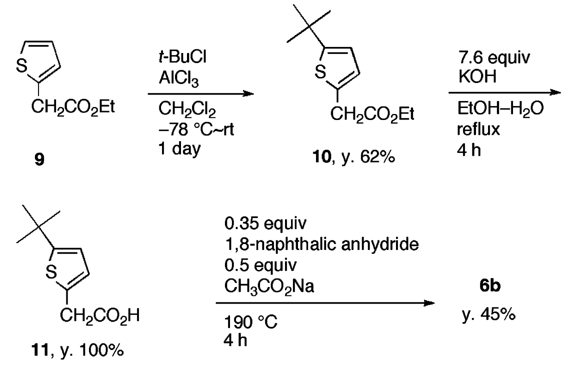


2. Results and discussion

2.1. Synthesis

2-Thienyl-3-hydroxyphenalenone (**6a**) was prepared by following the procedure described in the literature.[7] (5-*tert*-Butylthienyl)-3-hydroxyphenalenone (**6b**) was synthesized according to the method depicted in Scheme 1. Ester derivative **10** was obtained in 62% yield by introduction of *tert*-butyl group into a thiophene moiety of **9**.[8] Hydrolysis of **10** with KOH in EtOH–H_2O gave an acid derivative **11** in quantitative yield. The condensation reaction of **11** with 1,8-naphthalic anhydride in the presence of sodium acetate at 190 °C gave the 3-hydroxyphenalenone derivative **6b**.



Scheme 1.

Oxidation of **6a** and **6b** with a variety of organic or inorganic oxidants gave dimeric compounds **7** as a dark red powder and **8** as a yellow powder, respectively (Table 1).[9] The dimer **7** was obtained in low yields in the case of entries 1–5, however, use of 2,3-dichloro-5,6-dicyanoquinodimethane (DDQ) as an oxidant gave the highest yield (40%, entry 5). In contrast, the dimer **8** was obtained in high yields (70–98%) in all cases (entries 6–9).

Table 1. Synthesis of dimeric compounds **7** and **8**

$$\mathbf{6a, b} \xrightarrow{\text{oxidant}} \mathbf{7, 8}$$

Entry	6	Oxidant, equiv	Condition	Yield (%)
1[a]	**a**	PbO_2, 21	rt, 24 h	**7**, 15
2[a]	**a**	Ag_2CO_3, 20	rt, 25.5 h	**7**, 21
3[b]	**a**	Alkalic $K_3[Fe(CN)_6]$, 22	rt, 40 h	**7**, 29
4	**a**	*p*-Benzoquinone, 4.8	rt, 15 min; reflux, 3.5 h	**7**, 21
5[a]	**a**	DDQ, 9.5	rt, 10 min	**7**, 40
6[a]	**b**	PbO_2, 10	rt, 1 h	**8**, 70
7[a]	**b**	Ag_2CO_3, 5.1	rt, 1 h	**8**, 98
8[a]	**b**	*p*-Benzoquinone, 4.6	rt, 1 h	**8**, 87
9[a]	**b**	DDQ, 4.7	rt, 1 h	**8**, 79

[a] In benzene.

[b] In 10:1 benzene–H_2O.

2.2. Structural determination of 7 and 8

The dimeric structures of **7** and **8** have unambiguously been determined by a combination of FABMS, IR spectra, and ^1H, ^{13}C, HMQC, HMBC, and NOESY NMR spectra.[10]

The dimeric structure of **7** is depicted in Fig. 1a. FABMS of **7** gave *m*/*z* 552, indicating elimination of two protons from two molecules of 3-oxophenalenoxyl radical **5a**. ^1H NMR spectrum revealed that these protons originated from the thienyl moieties. ^{13}C NMR spectrum showed a downfield shift of one thienyl carbon (175.3 ppm) from the other thienyl carbons (102.5–148.6 ppm), indicating that the carbon atom on a thienyl ring is linked with an oxygen atom (Fig. 1a and Table 2). Furthermore, a long-range coupling between 6-proton and 9-carbon was observed in HMBC

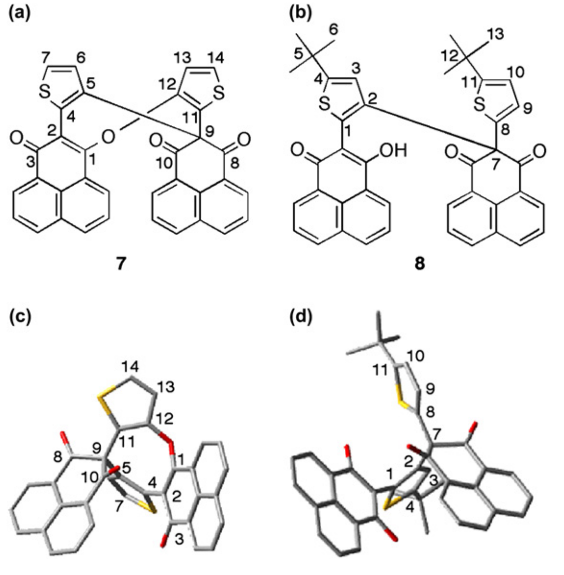


Figure 1. Chemical structures of **7** (a) and **8** (b), and optimized structures of **7** (c) and **8** (d) calculated by *Gaussian 03* at the B3LYP/6-31G(d,p) level of theory.[12]

Table 2. Observed and calculated ^1H and ^{13}C chemical shifts of **7**

Atom	Chemical shift, ppm		Atom	Chemical shift, ppm	
	Obsd[a]	Calcd[b]		Obsd[a]	Calcd[b]
H(6)	7.42	6.80	C(6)	128.7	121.4
H(7)	6.84	7.06	C(7)	121.0	127.5
H(13)	8.88	7.22	C(8)	182.8	188.7
H(14)	7.35	7.27	C(9)	111.8	76.1
C(1)	156.7	159.8	C(10)	184.9	190.9
C(2)	123.7	123.3	C(11)	102.5	122.6
C(3)	180.6	176.6	C(12)	175.3	149.3
C(4)	129.0	140.3	C(13)	134.0	115.7
C(5)	125.6	127.8	C(14)	148.6	125.3

[a] These chemical shifts were assigned by HMBC and HMQC measurements in $CDCl_3$ solution at 30 °C.[10]

[b] These values were calculated at the B3LYP/6-31G(d,p).

Table 3. Observed and calculated ^1H and ^{13}C chemical shifts of **8**

Atom	Chemical shift, ppm		Atom	Chemical shift, ppm	
	Obsd[a]	Calcd[b]		Obsd[a]	Calcd[b]
H(3)	6.64	7.09	C(5)	35.5	38.3
H(6)	1.37	1.30	C(6)	32.2	30.1
H(9)	5.83	6.60	C(7)	71.4	77.8
H(10)	6.65	6.73	C(8)	131.8	143.7
H(13)	0.39	1.49	C(9)	122.2	120.2
C(1)	141.9	133.2	C(10)	130.2	114.7
C(2)	123.1	134.1	C(11)	161.2	157.3
C(3)	124.8	122.0	C(12)	34.4	37.8
C(4)	163.6	159.7	C(13)	31.3	31.3

[a] These chemical shifts were assigned by HMBC, HMQC, and NOESY measurements in CD_2Cl_2–CF_3CO_2H solution at 30 °C.[10]

[b] These values were calculated at the B3LYP/6-31G(d,p).

spectra. These results reveal that the dimeric structure of **7** possesses an ether bond between the oxygen atoms at the 1-position and 12-position, and a C–C bond between the 5- and 9-positions (Fig. 1a).

The dimeric structure of **8** is shown in Figure 1b. FABMS of **8** gave *m*/*z* 666, which is equal to two molecules of **5b**. An absorption band due to a hydroxyl group was observed in an IR spectrum measured in a CCl_4 solution (1.1×10^{-3} M).[10] ^1H NMR showed the disappearance of a thienyl proton and upfield shift of protons of a *tert*-butyl group (0.39 ppm) from the other one (1.37 ppm). NOESY correlation was observed between a thienyl proton and a proton on a 3-oxophenalenoxyl moiety.[11] On the basis of these spectroscopic results, the dimeric structure of **8** was determined, having a C–C bond between the 2- and 7-positions (Fig. 1b).

The dimeric structures of **7** and **8** showed that their dimerizing positions are on their thienyl moieties. In order to elucidate a stereoelectronic effect on the structural difference between these dimers, we have calculated both the optimized structures and chemical shifts of **7** and **8** by *Gaussian 03* at B3LYP/6-31G(d,p) level of theory (Fig. 2c and d; Tables 2 and 3).[12] The calculated chemical shifts are in good agreement with the observed ones.[13] The dimer **7** has a thiophene-fused eight-membered ring structure formed by two-step dimerization reactions (Fig. 1c), which may indicate a low steric hindrance around the reactive site. In contrast, the dimer **8** has a C–C bond only between the 2- and 7-positions, which indicates a fairly large steric hindrance inhibiting an intramolecular formation of another bond. Considering that the upfield shift of *tert*-butyl protons H(13) was due to a ring-current effect of the opposite 3-oxophenalenoxyl ring, a steric effect of the *tert*-butyl groups seems to be the main factor.

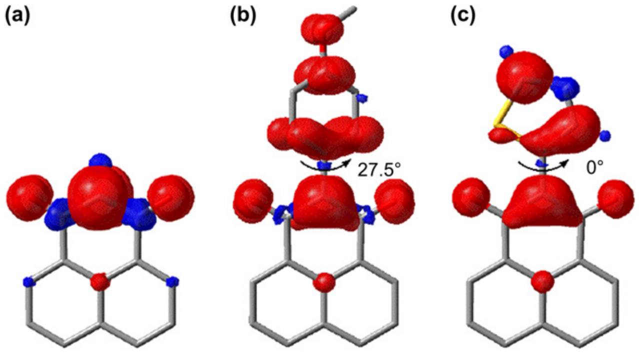


Figure 2. Spin density distributions of 3-oxophenalenoxyl (a), **3** (b), and **5a** (c) calculated by Gaussian 03 at the UBLYP/6-31G(d,p) level of theory.[12] Red and blue robes denote positive and negative spin densities, respectively.

These NMR studies reveal that the structures of **7** and **8** are formed by dimerization reactions at the carbon atoms on their thienyl moieties, indicating the occurrence of a considerable amount of spin-delocalization into the 2-substituted-thienyl moieties of **5a** and **5b**.

2.3. Spin density distributions of 3-oxophenalenoxyls

We have calculated the spin density distribution of 3-oxophenalenoxyl,[5a] *p*-methoxyphenyl derivative **3**,[6b] and **5a**[14] at the UBLYP/6-31G(d,p) level of theory (Fig. 2). These calculations indicate that **5a** possesses a co-planar structure between the 3-oxophenalenoxyl and thiophene skeletons, and a smaller spin density on the 2-position (ρ_2) than 3-oxophenalenoxyl and **3** (Fig. 2c and Table 4). In order to evaluate the degree of spin-delocalization into the thienyl moieties of **5a**, we have made summation of the absolute spin densities on the 3-oxophenalenoxyl moieties ($\Sigma|\rho_{3\text{-oxo}}|$) and the 2-substituted π-systems ($\Sigma|\rho_{2\text{-sub}}|$) (Table 4).[15] These results showed that the percentages of spin-delocalization into the 2-substituted π-systems were 35% for **3** and 50% for **5a**, illustrating that there occurs a larger amount of spin-delocalization of **5a** into the 2-substituted π-systems than that of **3**. These electronic-spin structures combined with stereoelectronic effects are responsible for the difference of the dimeric structures of **4** and **7**, **8**.

Table 4. Spin densities at the 2-position (ρ_2), sum of absolute spin densities on the 3-oxophenalenoxyl moieties ($\Sigma|\rho_{3\text{-oxo}}|$) and on the 2-substituted π-systems ($\Sigma|\rho_{2\text{-sub}}|$) calculated for 3-oxophenalenoxyl, **3**, and **5a** at the UBLYP/6-31G(d,p) level of theory

Compound	ρ_2	$\Sigma\lvert\rho_{3\text{-oxo}}\rvert$, %[a]	$\Sigma\lvert\rho_{2\text{-sub}}\rvert$, %[a]
3-Oxophenalenoxyl	+0.687	1.443, 100	—
3	+0.401	0.780, 65	0.425, 35
5a	+0.321	0.593, 50	0.593, 50

[a] Percentage of sum of absolute spin densities to total absolute spin densities ($\Sigma|\rho_{3\text{-oxo}}|+\Sigma|\rho_{2\text{-sub}}|$).

3. Conclusion

We have succeeded in increasing the spin-delocalization into the thienyl moieties with the decrease in the spin densities at the 2-positions of 2-thienyl-substituted 3-oxophenalenoxyl derivatives **5a** and **5b**. Their spin structures feature in the corresponding dimeric structures **7** and **8** and the spin density distributions acquired by DFT calculations. The dimeric structures of **7** and **8** have been determined by a combination of FABMS, IR, and NMR spectra, revealing that these dimers form bonds at the carbon atoms of their thienyl moieties. The DFT calculation of **5a** has exhibited a considerable amount of spin-delocalization into the thienyl moiety and correspondingly the decrease of the spin density at the 2-position. This study demonstrates an effective manipulation of the degree of spin-delocalized nature of open-shell π-electronic systems by invoking functional substitution, and provides important criteria to design novel spin-delocalized π-radicals for realization of novel spin-mediated molecular functional materials.

4. Experimental

4.1. General

^{1}H and ^{13}C NMR spectra were measured at 270 and 600 MHz with $CDCl_3$ or CD_2Cl_2–CF_3COOH as solvent and Me_4Si or residual solvents as internal standards. Correlation NMR spectra (HMBC, HMQC, and NOESY) were measured at 600 MHz with $CDCl_3$ or CD_2Cl_2–CF_3COOH as solvent and Me_4Si or residual solvents as internal standards. Infrared spectra were recorded using KBr plates, CCl_2CCl_2 or CCl_4 solution. EIMS spectra were recorded at 70 eV, and 3-nitrobenzyl alcohol was used as matrix for FABMS spectra. Elemental analyses were performed at the Graduate School of Science, Osaka University. Bulb-to-bulb short-path distillation was performed by using a glass tube oven (Kugelrohr). Silica gel 60 (100–200 mesh) was used for column chromatography. R_f values on TLC were recorded on E. Merck precoated (0.25 mm) silica gel 60 F_{254} plates. The plates were sprayed with a solution of 10% phosphomolybdic acid in 95% EtOH and then heated until the spots became clearly visible. Deactivated silica gel was prepared by mixing with 6% water. CH_2Cl_2, *tert*-butyl chloride, and benzene were dried over CaH_2 and distilled under argon prior to use. EtOH was dried over molecular sieves prior to use. 2-Thienyl-3-hydroxyphenalenone (**6a**)[7] and active PbO_2[16] were prepared and purified by the procedure described in the literatures. Ethyl 2-thienylacetate **9** was prepared by esterification of commercially available 2-thienylacetic acid in EtOH in the presence of concd H_2SO_4. 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) was purified by recrystallization of purchased material from $CHCl_3$. Other reagents were used without purification. All reactions requiring anhydrous conditions were conducted under an argon atmosphere.

4.2. Synthesis of dimeric compound 7

4.2.1. Oxidation with PbO_2. 3-Hydroxyphenalenone derivative **6a** (21 mg, 0.076 mmol) was placed in a 50-mL round-bottomed flask and dissolved with benzene (30 mL) under an argon atmosphere. To the mixture was added PbO_2 (381 mg, 1.59 mmol), and the mixture was stirred overnight at room temperature. The reaction mixture was filtered through Celite column and washed with $CHCl_3$ and concentrated under reduced pressure. The residue was subjected to column chromatography with CH_2Cl_2 as an eluant to give dimer **7** (6.2 mg, 15%).

4.2.2. Oxidation with Ag_2CO_3. Compound **6a** (19 mg, 0.069 mmol) was placed in a 50-mL round-bottomed flask and dissolved with benzene (30 mL) under an argon atmosphere. To the mixture was added Ag_2CO_3 (371 mg, 1.35 mmol), and the mixture was stirred overnight at room temperature. The reaction mixture was filtered through Celite column and washed with $CHCl_3$ and concentrated under reduced pressure. The residue was subjected to column chromatography with CH_2Cl_2 as an eluant to give **7** (3.9 mg, 21%).

4.2.3. Oxidation with $K_3[Fe(CN)_6]$. Compound **6a** (20 mg, 0.070 mmol) was placed in a 50-mL round-bottomed flask and dissolved with benzene (30 mL) under an argon atmosphere. To the mixture was added $K_3[Fe(CN)_6]$ (510 mg, 1.6 mmol, in potassium hydroxide aqueous solution, 5 mL), and the mixture was stirred at room temperature for 2 days. The organic layer was separated and dried over Na_2SO_4, then filtered, and concentrated under reduced pressure to give **7** (6 mg, 29%).

4.2.4. Oxidation with *p*-benzoquinone. Compound **6a** (19.0 mg, 0.068 mmol) was placed in a 50-mL round-bottomed flask and dissolved with benzene (30 mL) under an argon atmosphere. To the mixture was added *p*-benzoquinone (34 mg, 0.31 mmol), and the mixture was stirred at room temperature for 6 h and refluxed for 1.5 h. The reaction mixture was concentrated and subjected to column chromatography with CH_2Cl_2 as an eluant to give **7** (4 mg, 21%).

4.2.5. Oxidation with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ). Compound **6a** (19 mg, 0.068 mmol) was placed in a 50-mL round-bottomed flask and dissolved with benzene (30 mL) under an argon atmosphere. To the mixture was added DDQ (145 mg, 0.64 mmol), and the mixture was stirred at room temperature for 10 min. The reaction mixture was filtered and the residue was rinsed with benzene. The solution was concentrated under reduced pressure and subjected to column chromatography with CH_2Cl_2 as an eluant to give **7** (8 mg, 40%).

4.2.6. Physical data of dimer 7. A dark red powder. Mp 272–273 °C, TLC R_f 0.29 (CH_2Cl_2); ^{1}H NMR (600 MHz, $CDCl_3$) δ_H 6.84 (1H, d, J=5.3 Hz), 7.35 (1H, d, J=6.3 Hz), 7.42 (1H, d, J=5.3 Hz), 7.61 (1H, t, J=7.8 Hz), 7.70 (1H, t, J=7.8 Hz), 7.77 (1H, t, J=8.3 Hz), 7.82 (1H, t, J=7.9 Hz), 8.08 (1H, d, J=8.3 Hz), 8.19 (1H, d, J=7.3 Hz), 8.21 (2H, d, J=7.9 Hz), 8.28 (1H, dd, J=7.3 and 1.0 Hz), 8.53 (1H, dd, J=7.3 and 1.0 Hz), 8.65 (1H, dd, J=6.9 and 1.3 Hz), 8.75 (1H, dd, J=7.3 and 1.0 Hz), 8.88 (1H, d, J=6.3 Hz); ^{13}C NMR (600 MHz, $CDCl_3$) δ 184.9 (C), 182.8 (C), 180.6 (C), 175.3 (C), 156.7 (C), 148.6 (CH), 135.2 (C), 134.2 (CH), 134.1 (CH), 134.0 (CH), 133.1 (CH), 132.6 (C), 131.8 (C), 130.7 (CH), 129.9 (C), 129.6 (CH), 129.5 (CH), 129.0 (C), 128.7 (CH), 127.8 (C), 127.7 (CH), 127.1 (CH), 127.1 (C), 126.7 (CH), 126.7 (CH), 126.6 (CH), 125.9 (C), 125.6 (C), 123.7 (C), 123.0 (C), 121.0 (CH), 111.8 (C), 102.5 (C); IR (KBr) (ν_{max}) 1655, 1634, 1605, 1578 cm^{-1}; IR (CCl_4) (ν_{max}) 1638 cm^{-1}; FABMS, *m/z* 552 (M^+).

4.3. Synthesis of dimeric compound 8

4.3.1. Ethyl 5-*tert*-butyl-2-thienylacetate (10). $AlCl_3$ (3.60 g, 27.0 mmol) was placed in a 50-mL round-bottomed flask and suspended with CH_2Cl_2 (6 mL). After cooling to −78 °C, CH_2Cl_2 (3 mL) solution of ethyl 2-thienylacetate **9** (4.60 g, 27.0 mmol) was added over 5 min to this mixture and then stirred at this temperature for 5 min. CH_2Cl_2 solution (3 mL) of *tert*-butyl chloride (3.0 mL, 27.6 mmol) was added over 15 min to this mixture, and stirred at −78 °C for 1 h. This reaction mixture was gradually warmed up to room temperature and stirred at this temperature for 24 h. This reaction mixture was poured into ice-water, and then organic layer was separated. Aqueous layer was extracted with CH_2Cl_2 (20 mL×2). The combined organic layers were washed with H_2O (40 mL), 1% KOH aq (30 mL), and H_2O (30 mL), successively. The resulting organic layer was dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residual oil was subjected bulb-to-bulb short-path distillation (Kugelrohr) to yield *tert*-butylated ester **10** (3.76 g, 62%) as colorless oil. TLC R_f 0.47 (benzene); ^{1}H NMR (270 MHz, $CDCl_3$) δ_H 1.28 (3H, t, J=7.1 Hz), 1.36 (9H, s), 3.75 (2H, d, J=1.0 Hz), 4.18 (2H, q, J=7.2 Hz), 6.65 (1H, d, J=3.3 Hz), 6.72 (1H, d, J=3.3 Hz).

4.3.2. 5-*tert*-Butyl-2-thienylacetic acid (11). *tert*-Butylated ethyl ester **10** (3.76 g, 16.6 mmol) was placed in a 100-mL round-bottomed flask and dissolved with EtOH (30 mL). To this mixture was added aqueous (20 mL) solution of KOH (7.05 g, 126 mmol) and refluxed for 9 h. After most of EtOH was removed by distillation, concd HCl was added at room temperature. The reaction mixture was poured into a H_2O and extracted with CH_2Cl_2. The organic extracts were dried over Na_2SO_4, filtered, and concentrated under reduced pressure to give almost pure carboxylic acid **11** (3.34 g, 100%) as a light yellow oil. TLC R_f 0.51 (ethyl acetate); ^{1}H NMR (270 MHz, $CDCl_3$) δ_H1.36 (9H, s), 3.81 (2H, d, J=1.0 Hz), 6.67 (1H, d, J=3.6 Hz), 6.75 (1H, d, J=3.6 Hz).

4.3.3. 2-(5-*tert*-Butylthienyl)-3-hydroxyphenalenone (6b). 1,8-Naphthalic anhydride (1.14 g, 5.75 mmol) was placed in a 30-mL round-bottomed flask and mixed with *tert*-butylated thienylacetic acid **11** (3.34 g, 16.8 mmol) and NaOAc (0.72 g, 8.73 mmol), and then stirred at 190 °C for 4 h. After cooling to room temperature, the reaction mixture was directly subjected to deactivated silica gel column chromatography with benzene as an eluant to give **6b** (0.87 g, 45%) as a purple solid. TLC R_f 0.41 (CH_2Cl_2); ^{1}H NMR (270 MHz, $CDCl_3$) δ_H 1.45 (9H, s), 6.93 (1H, d, J=3.6 Hz), 7.02 (1H, s), 7.09 (1H, d, J=3.6 Hz), 7.68 (1H, dd, J=8.3 and 7.3 Hz), 7.76 (1H, dd, J=8.1 and 7.4 Hz), 8.10 (1H, dd, J=8.3 and 1.0 Hz), 8.18 (1H, dd, J=8.1 and 1.2 Hz), 8.36 (1H, dd, J=7.3 and 1.3 Hz), 8.65 (1H, dd, J=7.4 and 1.2 Hz); IR (KBr) (ν_{max}) 3456, 3070, 2962, 1630, 1603, 1553 cm^{-1}; IR (CCl_2CCl_2) (ν_{max}) 3460, 3063, 2966, 1642, 1585 cm^{-1}; EIMS, *m/z* (%) 334 (M^+, 39), 319 (M^+-CH_3, 100).

4.3.4. Oxidation with PbO_2. 3-Hydroxyphenalenone derivative **6b** (294 mg, 0.88 mmol) was placed in a 50-mL round-bottomed flask and dissolved with benzene (300 mL) under an argon atmosphere. To the mixture was added PbO_2 (2.08 g, 8.70 mmol), and the mixture was stirred at room temperature for 1 h. The reaction mixture was filtered through Celite column and the residue was rinsed with $CHCl_3$. The solution was concentrated under reduced pressure and subjected to column chromatography with 100:1 mixture of CH_2Cl_2 and ethyl acetate as an eluant to give dimer **8** (205 mg, 70%).

4.3.5. Oxidation with Ag_2CO_3. Compound **6b** (29 mg, 0.087 mmol) was placed in a 50-mL round-bottomed flask and dissolved with benzene (30 mL) under an argon atmosphere. To the mixture was added Ag_2CO_3 (124 mg, 0.45 mmol), and the mixture was stirred at room temperature for 1 h. The reaction mixture was filtered through Celite column and the residue was rinsed with $CHCl_3$. The solution was concentrated under reduced pressure to give **8** (28 mg, 98%).

4.3.6. Oxidation with *p*-benzoquinone. Compound **6b** (19 mg, 0.056 mmol) was placed in a 50-mL round-bottomed flask and dissolved with benzene (15 mL) under an argon atmosphere. To the mixture was added *p*-benzoquinone (28 mg, 0.26 mmol), and the mixture was stirred at room temperature for 1 h. The reaction mixture was concentrated and subjected to column chromatography with CH_2Cl_2 as an eluant to give **8** (16 mg, 87%).

4.3.7. Oxidation with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ). Compound **6b** (19 mg, 0.057 mmol) was placed in a 50-mL round-bottomed flask and dissolved with benzene (15 mL) under an argon atmosphere. To the mixture was added DDQ (60 mg, 0.27 mmol), and the mixture was stirred at room temperature for 1 h. The reaction mixture was filtered and the residue was rinsed with benzene. The solution was concentrated under reduced pressure and subjected to column chromatography with CH_2Cl_2 as an eluant to give **8** (15 mg, 79%).

4.3.8. Physical data of dimer 8. Yellow powder. Mp 197–198 °C; TLC R_f 0.53 (1:1 hexane–ethyl acetate); ^{1}H NMR (270 MHz, CD_2Cl_2–CF_3COOH) δ_H 0.39 (9H, s), 1.37 (9H, s), 5.83 (1H, d, J=4.0 Hz), 6.64 (1H, s), 6.65 (1H, d, J=4.0 Hz), 7.86 (2H, dd, J=8.3 and 7.3 Hz), 7.99 (2H, t, J=7.8 Hz), 8.38 (2H, dd, J=8.4 and 1.2 Hz), 8.59 (2H, dd, J=8.3 and 1.0 Hz), 8.69 (2H, dd, J=7.3 and 1.3 Hz), 8.93 (2H, dd, J=7.8 and 1.2 Hz); ^{13}C NMR (600 MHz, CD_2Cl_2–CF_3COOH) δ_C 195.6 (C), 175.6 (C), 163.6 (C), 161.2 (C), 141.9 (C), 140.4 (C), 137.2 (CH), 135.7 (CH), 133.3 (C), 132.3 (CH), 131.8 (CH), 131.5 (C), 130.2 (CH), 128.6 (CH), 127.7 (CH), 126.2 (C), 125.5 (C), 124.8 (CH), 123.1 (C), 122.2 (CH), 71.4 (C), 35.5 (C), 34.4 (C), 32.2 (CH_3), 31.3 (CH_3); IR (KBr) (ν_{max}) 3444, 3062, 2961, 1686, 1655, 1638, 1578 cm^{-1}; IR (CCl_4) (ν_{max}) 3313, 2965, 1669, 1742, 1702, 1669, 1640 cm^{-1}; EIMS, *m/z* (%) 666 (M^+, 31%); FABMS, *m/z*, 666 (M^+); Anal. Calcd (%) for $C_{42}H_{34}O_4S_2$: C, 75.65; H, 5.14; N, 0.00. Found: C, 75.36; H, 5.25; N, 0.00.

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Supplementary data

^{1}H, ^{13}C, HMQC, and HMBC NMR spectra, IR spectra, calculated ^{1}H and ^{13}C chemical shifts of **7** and **8**, NOESY NMR spectrum of **8**, observed and calculated ^{1}H and ^{13}C chemical shifts of **4**, and the result of DFT calculation of spin density distribution of **5a**. Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.tet.2007.05.018.

References and notes

1. For recent overview of molecule-based magnetic materials, see, e.g.: (a) *Molecular Magnetism*; Itoh, K., Kinoshita, M., Eds.; Kodansha, and Gordon and Breach Science: Tokyo, 2000; (b) *Magnetic Properties of Organic Materials*; Lahti, P. M., Ed.; Marcel Dekker: New York, NY, 1999; (c) Kahn, O., Ed.; *Mol. Cryst. Liq. Cryst.* **1999**, *334/335* 1–712/1–706; (d) Itoh, K., Miller, J. S., Takui, T., Eds.; *Mol. Cryst. Liq. Cryst.* **1997**, *305/306* 1–586/1–520; (e) Rajca, A.; Wongsriratanakul, J.; Rajca, S. *Science* **2001**, *294*, 1503–1505; (f) Itoh, K.; Takui, T. *Proc. Jpn. Acad., Ser. B* **2004**, *80*, 29–40.
2. (a) Itkis, M. E.; Chi, X.; Cordes, A. W.; Haddon, R. C. *Science* **2002**, *296*, 1443–1445; (b) Pal, S. K.; Itkis, M. E.; Tham, F. S.; Reed, R. W.; Oakley, R. T.; Haddon, R. C. *Science* **2005**, *309*, 281–284; (c) Tsubata, Y.; Suzuki, T.; Miyashi, T.; Yamashita, Y. *J. Org. Chem.* **1992**, *52*, 6749–6755; (d) Kubo, T.; Shimizu, A.; Sakamoto, M.; Uruichi, M.; Yakushi, K.; Nakano, M.; Shiomi, D.; Sato, K.; Takui, T.; Morita, Y.; Nakasuji, K. *Angew. Chem., Int. Ed.* **2005**, *44*, 6564–6568.
3. (a) Morita, Y.; Aoki, T.; Fukui, K.; Nakazawa, S.; Tamaki, K.; Suzuki, S.; Fuyuhiro, A.; Yamamoto, K.; Sato, K.; Shiomi, D.; Naito, A.; Takui, T.; Nakasuji, K. *Angew. Chem., Int. Ed.* **2002**, *41*, 1793–1796; (b) Suzuki, S.; Morita, Y.; Fukui, K.; Sato, K.; Shiomi, D.; Takui, T.; Nakasuji, K. *J. Am. Chem. Soc.* **2006**, *128*, 2530–2531.
4. (a) Morita, Y.; Ohba, T.; Haneda, N.; Maki, S.; Kawai, J.; Hatanaka, K.; Sato, K.; Shiomi, D.; Takui, T.; Nakasuji, K. *J. Am. Chem. Soc.* **2000**, *122*, 4825–4826; (b) Morita, Y.; Maki, S.; Fukui, K.; Ohba, T.; Kawai, J.; Sato, K.; Shiomi, D.; Takui, T.; Nakasuji, K. *Org. Lett.* **2001**, *3*, 3099–3102; (c) Morita, Y.; Nishida, S.; Kawai, J.; Fukui, K.; Nakazawa, S.; Sato, K.; Shiomi, D.; Takui, T.; Nakasuji, K. *Org. Lett.* **2002**, *4*, 1985–1988; (d) Morita, Y.; Kawai, J.; Nishida, S.; Haneda, N.; Fukui, K.; Sato, K.; Shiomi, D.; Takui, T.; Nakasuji, K. *Synth. Met.* **2003**, *137*, 1217–1218; (e) Nishida, S.; Morita, Y.; Fukui, K.; Sato, K.; Shiomi, D.; Takui, T.; Nakasuji, K. *Angew. Chem., Int. Ed.* **2005**, *44*, 7277–7280.
5. (a) Morita, Y.; Kawai, J.; Fukui, K.; Nakazawa, S.; Sato, K.; Shiomi, D.; Takui, T.; Nakasuji, K. *Org. Lett.* **2003**, *5*, 3289–3291; (b) Morita, Y.; Kawai, J.; Nishida, S.; Fukui, K.; Nakazawa, S.; Sato, K.; Shiomi, D.; Takui, T.; Nakasuji, K. *Polyhedron* **2003**, *22*, 2205–2208.
6. (a) Hatanaka, K.; Morita, Y.; Ohba, T.; Yamaguchi, K.; Takui, T.; Kinoshita, M.; Nakasuji, K. *Tetrahedron Lett.* **1996**, *37*, 873–876; (b) Morita, Y.; Nishida, S.; Fukui, K.; Hatanaka, K.; Ohba, T.; Sato, K.; Shiomi, D.; Takui, T.; Yamamoto, G.; Nakasuji, K. *Polyhedron* **2005**, *24*, 2194–2199.
7. Minchev, S.; Stoyanov, N. M.; Kashchieva, M. V.; Miteva, M. I.; Alexiev, B. V. *Dokl. Bulg. Akad. Nauk.* **1992**, *45*, 45–48.
8. Ester **10** was prepared according to the method of *tert*-butylation of thiophene, see: Belen'kii, L. I.; Yakubov, A. P. *Tetrahedron* **1984**, *40*, 2471–2477.
9. Oxidation of 3-hydroxyphenalenone derivatives **6a** and **6b** with PbO_2 in 1-methylnaphthalene between 30–170 °C in sealed ESR tubes gave no ESR signals of the corresponding neutral radicals **5a** and **5b**.
10. IR and NMR spectra are shown in Supplementary data.
11. NOESY spectra of **8** showed a correlation between the proton in 10-position and those in the opposite 3-oxophenalenoxyl moiety; see, Supplementary data.
12. Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian 03, Revision B.05*; Gaussian: Wallingford, CT, 2004.
13. In the dimer **4**, values of observed ^{1}H and ^{13}C chemical shifts were in good agreement with calculated one based on X-ray crystal structure, see, Supplementary data.
14. The calculated spin density distribution of **5a** is summarized in Supplementary data.
15. This method was proposed in our previous study, see: Fukui, K.; Morita, Y.; Nishida, S.; Kobayashi, T.; Sato, K.; Shiomi, D.; Takui, T.; Nakasuji, K. *Polyhedron* **2005**, *24*, 2326–2329.
16. (a) Kuhn, R.; Hammer, I. *Chem. Ber.* **1950**, *83*, 413–414; (b) Wilmarth, W. K.; Schwartz, N. *J. Am. Chem. Soc.* **1955**, *77*, 4543–4545.