JACS
JOURNAL OF THE AMERICAN CHEMICAL SOCIETY
COMMUNICATION
pubs.acs.org/JACS

Air- and Heat-Stable Planar Tri-*p*-quinodimethane with Distinct Biradical Characteristics

Xiaozhang Zhu, Hayato Tsuji,* Koji Nakabayashi, Shin-ichi Ohkoshi, and Eiichi Nakamura*

Department of Chemistry, School of Science, The University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113-0033, Japan

Supporting Information

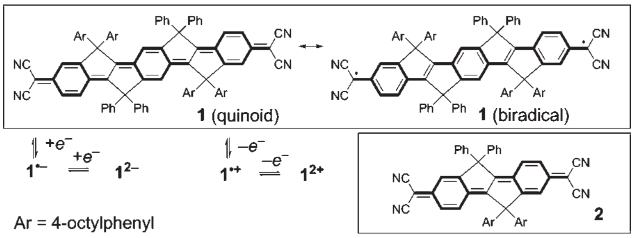
ABSTRACT: A heptacyclic carbocycle possessing three *p*-quinodimethane units conjugated in one plane has been synthesized and shown to exhibit distinct biradical characteristics. The molecule has a HOMO/LUMO band gap of ca. 1 eV and a S_0-T_1 energy gap of 2.12 kcal/mol, and it absorbs and emits near-IR light at room temperature. It is air-stable under ambient light for several months and thermally stable up to 160 °C under nitrogen, and it undergoes reversible two-electron oxidation and reduction. The synthetic approach is such that a smaller and larger oligo-*p*-quinodimethane can be synthesized.

Non-Kekulé or biradicaloid molecules, of which trimethylenemethane[1] and quinodimethane (QM)[2] are classical examples, have been the subject of interest for 100 years[3] because of their diverse chemical and physical properties;[4] however, their instability has remained a challenge for those who aim at their applications. We report here that a heptacyclic tri-*p*-quinodimethane **1** (tri-*p*-QM) shows a distinct biradical character but is by far the most stable among biradicaloids known. For instance, it is air-stable under ambient light for several months, both as a solid and in solution, and undergoes facile and reversible two-electron reduction to give $\mathbf{1}^{2-}$ and oxidation to give $\mathbf{1}^{2+}$ (Scheme 1). The decomposition temperature under nitrogen is as high as >160 °C. The molecule has a very narrow band gap of ca. 1 eV, exhibiting a series of long-wavelength absorption bands extending to 1200 nm, and emits near-IR light at 1179 nm at room temperature—a rare example among biradicaloid molecules.[5] The molecule has a singlet open-shell ground state with a S_0-T_1 energy gap of 2.12 kcal/mol, as determined by SQUID measurements. As illustrated for the synthesis of **1** and its smaller congener **2** in Scheme 2, our synthetic approach can connect multiple *p*-QM units while keeping them fully conjugated and hence allows us to systematically study the correlation between the structure and the properties of biradicaloids.

The tri-*p*-QM **1** features three QM units connected by carbon bridges that secure the planarity of the whole π-system.[6] The four cyano groups on the conjugation termini lower the HOMO level and hence stabilize the biradicaloid against molecular oxygen. The 4-octyl side chains on the Ar groups were installed to increase the solubility and, together with other phenyl groups, may contribute to stabilization of the biradicaloid. To test the viability of our molecular design, we first synthesized a di-*p*-QM **2** (Scheme 2).

The synthesis of **2** started from the acetylene compound **3**, which was coupled in two steps with bis(4-octylphenyl)methanone (Ar_2CO) according to a published procedure to obtain the carbon-bridged stilbene **4** in 83% overall yield.[6] Bromination of **4** with $CuBr_2/Al_2O_3$[7] afforded exclusively a 3,8-dibromide that was then converted to the corresponding diiodide **5** in 95% yield (three steps). The diiodide **5** was coupled with sodium dicyanomethanide under palladium catalysis, and the product was oxidized with DDQ to obtain the desired di-*p*-QM **2** in 92% yield as a sky-blue solid (Figure 2, inset). Similarly, the tri-*p*-QM **1** was synthesized readily from the bisacetylene **6** via **7** and **8** and obtained as a green solid (Figure 2, inset). The compound was stable enough to be readily obtained as an analytically pure sample.

Scheme 1. Tri-*p*-quinodimethane, Dianion, and Dication

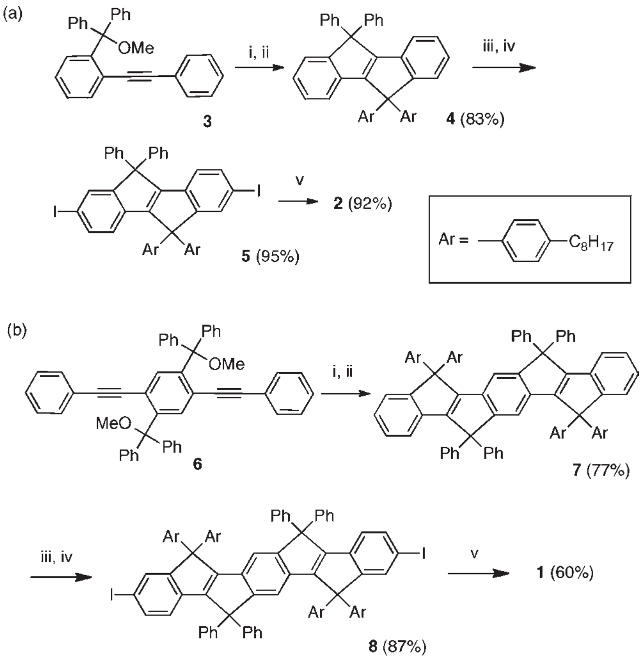


The ^{13}C and ^{1}H NMR spectra of di-*p*-QM **2** were well resolved and helped us to assign the structures, while those of tri-*p*-QM **1** were broadened by a contribution from the thermally excited triplet state. Thus, the ^{13}C NMR spectrum of **2** showed characteristic signals at δ 64.1 and 64.6 ppm because of the bridging sp^3 carbon atoms and at δ 81.1 and 81.2 ppm because of the $-C(sp^2)(CN)_2$ atoms. In contrast, compound **1** showed ^{13}C NMR signals only from the sp^3 carbon atoms in the carbon bridge and the *n*-octyl groups, and no discernible signals from the sp^2 carbon atoms. The ^{1}H NMR signals of **1** showed temperature-dependent broadening, suggesting the presence of thermally populated triplet species (see Supporting Information, Figure S12).

The magnetic properties of **1**, as examined by ESR and SQUID measurements (see Supporting Information), indicated that **1** has a biradical character with a singlet ground state, as illustrated in Scheme 1. The ESR spectrum of **1** at 340 K in the solid state exhibited a signal at $g = 2.003$ with a fine structure, suggesting the existence of a spin−spin interaction. The spin−spin distance was estimated by point dipole−dipole approximation to be 14.6 Å, which is very close to the distance between the two radicals in **1** and suggests the presence of an intramolecular spin−spin interaction of the triplet state. The energy gap between S_0 and T_1 states was determined to be 2.12 kcal/mol

Received: June 29, 2011
Published: September 20, 2011

Scheme 2. Synthesis of Di-*p*-QM (a) and Tri-*p*-QM (b)[a]



[a] Reagents and conditions: (i) Lithium naphthalenide, THF, bis(4-octylphenyl)methanone (Ar_2CO). (ii) $BF_3\cdot Et_2O$, CH_2Cl_2, 30 min. (iii) $CuBr_2/Al_2O_3$, CCl_4, 85 °C, overnight. (iv) (a) BuLi, Et_2O, 0 °C, 1 h; (b) Diiodoethane, 0.5 h. (v) Malononitrile, NaH, $Pd(PPh_3)_4$, THF, 70 °C, 8 h, followed by oxidation with Br_2/H_2O or DDQ.

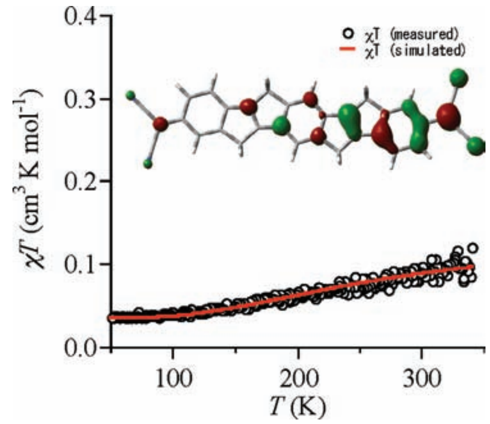


Figure 1. $\chi T-T$ plot of a solid sample of **1**. The fitting curve is drawn using the Bleaney−Bowers equation with a g value of 2.0, and diamagnetic susceptibility of -1.03×10^{-3} emu·mol^{-1}. The diamagnetic susceptibility was calculated according to Pascal's additive law. The estimated singlet−triplet energy gap (ΔE_{S-T}) is 2.12 kcal·mol^{-1}. Inset: One of the two singly occupied molecular orbitals of **1** calculated at the UB3LYP(BS)/6-31G** level, shown with isovalue 0.04 for the surfaces.

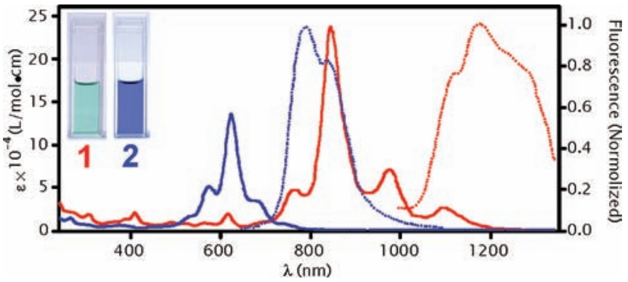


Figure 2. Absorption and emission spectra of **1** (red) and **2** (blue) in dichloromethane. Inset: Pictures of solutions of **1** and **2**.

(or 0.09 eV) by SQUID measurements (Figure 1). This gap is far smaller than the S_0—S_1 gap of 1.46 eV determined on the basis of the absorption spectrum (vide infra). Density functional theory calculations on a model system lacking the phenyl and aryl groups supported the biradical character. Calculations at the RB3LYP/6-31G** level of theory showed instability of the wave function, and the unrestricted broken-symmetry UB3LYP(BS) calculations indicated that an open-shell singlet biradical with spin contamination $\langle S^2 \rangle$ of 0.97 is lower in energy than the corresponding closed-shell singlet by 5.21 kcal/mol. The optimized geometries of singlet and triplet **1** are more similar than those in **2**, which is also in consistent with the greater diradical character in singlet **1**. The calculated S_0—T_1 energy gap was 1.83 kcal/mol, which is in good agreement with the above experimental value. One of the two singly occupied molecular orbitals of **1** in Figure 1 (inset) indicates higher electron density on the terminal atoms.

In contrast to **1**, the less extensively conjugated di-*p*-QM **2** did not show any ESR signal. The open-shell singlet with spin contamination $\langle S^2 \rangle$ of 0.64 was more stable than the closed-shell singlet by only 1.13 kcal/mol. The calculated S_0—T_1 energy gap (5.68 kcal/mol or 0.25 eV) was much larger than that of **1**, which is consistent with the well-resolved NMR spectra of **2** at room temperature. The S_0—S_1 gap was 1.98 eV, which is much larger than the S_0—T_1 energy gap.

Tri-*p*-QM **1** and di-*p*-QM **2** show different absorption and emission in the visible to near-IR regions, as shown in Figure 2 and Table 1. The tri-*p*-QM **1** exhibited a series of structured long-wavelength absorption bands extending to 1200 nm, with maximum absorption at 850 nm (red solid line). The optical bandgap determined on the basis of the absorption onset was 1.02 eV, which agrees with the value of 0.94 eV obtained by cyclic voltammetry (Table 1, last column). Notably, this compound emitted a near-IR light at 1179 nm (excited at 850 nm; quantum yield of 0.0032% using indocyanine green (ICG)[8]) at room temperature. The rigid and planar structure enabled the near-IR emission albeit in low quantum yield.

In contrast, the di-*p*-QM **2** absorbs visible light with a maximum at 627 nm (solid blue line) and emits in the near-IR region with a maximum at 792 nm (excited at 627 nm in dichloromethane; quantum yield of 0.14% using ICG[8]). The optical band gap was 1.58 eV, which agrees with the 1.54 eV value obtained by cyclic voltammetry. Not unexpectedly, the absorption maxima of **1** and **2** are more red-shifted than those of their aromatic precursors **7** and **4** by 454 and 292 nm, respectively (Supporting Information, Figure S7).

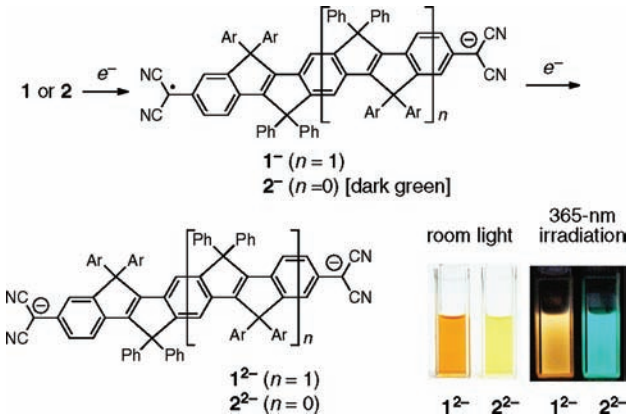
Finally, we describe the thermal and chemical properties of the new biradicaloids. First, both **1** and **2** are very thermally stable for biradicaloids. Thus, the tri-*p*-QM **1** is stable under nitrogen below 162 °C and gradually decomposes up to 287 °C with exothermicity of 16.9 kcal/mol (Supporting Information for the DSC trace). The di-*p*-QM **2** starts to melt at 155 °C (12.3 kcal/mol endothermic), which causes decomposition up to 250 °C, with 17.9 kcal/mol exothermicity. None of the decomposition products of either compound gave soluble materials.

Table 1. Photophysical and Electrochemical Properties of 1 and 2[a]

	λ_{abs}/nm[a] (ε/M^{-1} cm^{-1})	λ_{em}/nm[a] (Φ)	$E_{red}^{1/2}$/V[d]	$E_{ox}^{1/2}$/V[d]	E_g/eV[f]
1	769, 850 (5.37),[b] 980, 1100	1179 (3.2×10^{-5})[c]	−0.42, −0.47	0.52, 1.11	1.02 (0.94)[g]
$\mathbf{1}^{2-}$	459, 485 (4.75)	528 (0.91)[c]			2.36
2	578, 627 (5.12),[b] 683, 750	792 (1.4×10^{-3})[c]	−0.42, −0.61	1.12[(IR)e]	1.58 (1.54)[g]
$\mathbf{2}^{2-}$	420, 436 (4.38)	507 (0.60)[c]			2.64

[a] Measured in dichloromethane. [b] The absorption coefficients are given in logarithmic units. [c] Quantum yield using ICG as a reference. [d] Cyclic voltammetry on a carbon electrode with Bu$_4$NClO$_4$ in CH$_2$Cl$_2$ (0.1 M), corrected for ferrocene. [e] Irreversible. [f] Band gap determined from absorption onset. [g] Band gap determined from cyclic voltammetry.

Scheme 3. Reduction of Tri-*p*-QM 1 and Di-*p*-QM 2



Second, they are air-stable. For instance, the tri-*p*-QM **1** remained unchanged under air and ambient light for 6 months as a solid and over 2 months in solution, and it showed a half-life of 2 days, even in air-saturated dichloromethane under continuous UV irradiation (360 nm, 4 W).

Third, tri-*p*-QM **1** undergoes reversible, stepwise two-electron reduction and oxidation (Table 1), while **2** can be two-electron-reduced reversibly but oxidized only once and irreversibly. The HOMO levels of **1** and **2** estimated from the oxidation potential obtained by differential pulse voltammetry were quite deep: −5.32 eV (**1**) and −5.92 eV (**2**), partly accounting for the resistance to oxidation.

Fourth, chemical reduction of **1** and **2** gave a stable dianionic product. Comparison of the reduction potentials of **1** (−0.42 and −0.47 V, Table 1) and **2** (−0.42 and −0.61 V) suggests that **1** may be reduced directly to a dianion, while **2** may be reduced in a stepwise manner, which was indeed the case. Thus, we reduced **2** with a mild reducing agent, tetrabutylammonium borohydride (TBABH$_4$, 2 equiv) in anhydrous dichloromethane (Scheme 3).[9] Upon addition of TBABH$_4$ at room temperature, the blue color of **2** changed to dark green, suggestive of a radical anion $\mathbf{2}^{\cdot-}$ (λ_{max} 683 nm; spectrum in Supporting Information), and gradually to yellow (436 nm) of a dianion $\mathbf{2}^{2-}$, which exhibited green luminescence (507 nm, $\Phi = 0.60$; excitation at 420 nm). On the other hand, a green solution of **1** immediately changed to the orange-red (485 nm) of dianion $\mathbf{1}^{2-}$, which exhibited orange emission (528 nm, $\Phi = 0.91$; excitation at 459 nm). Such high-efficiency emission is characteristic of the parent planar phenylenevinylene motif.[6]

In summary, we have synthesized carbon-bridged tri-*p*-QM compound **1**, which exhibits distinctive biradical characteristics, and its di-*p*-QM analogue **2**, which exhibits similar characteristics. In view of the availability of methods to synthesize similar carbon networks bridged by heteroatoms connected with a different connectivity,[10,11] we expect that this new molecular design will allow us to study systematically the fundamental and applied aspects of biradicaloid molecules for research on nonlinear optics[12] and organic electronics.[13]

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. Experimental details. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

tsuji@chem.s.u-tokyo.ac.jp; nakamura@chem.s.u-tokyo.ac.jp

■ ACKNOWLEDGMENT

This Communication is dedicated to Prof. Christian Bruneau on the occasion of his 60th birthday. We thank MEXT for financial support (KAKENHI for E.N., No. 22000008; H.T., No. 20685005; and the Global COE Program for Chemistry Innovation). This work was partly supported by the Strategic Promotion of Innovative R&D, JST. Z.X. thanks the JSPS Postdoctoral Fellowship for Foreign Researchers (No. P 09046).

■ REFERENCES

(1) (a) Dowd, P. *Acc. Chem. Res.* **1972**, *5*, 242. (b) Yamago, S.; Nakamura, E. *Org. React.* **2002**, *61*, 1.

(2) Szwarc, M. *Discuss. Faraday Soc.* **1947**, *2*, 46.

(3) (a) Thiele, J.; Balhorn, H. *Chem. Ber.* **1904**, *37*, 1463. (b) Chichibabin, A. E. *Chem. Ber.* **1907**, *40*, 1810.

(4) (a) Takahashi, T.; Matsuoka, K.-I.; Takimiya, K.; Otsubo, T.; Aso, Y. *J. Am. Chem. Soc.* **2005**, *127*, 8928. (b) Ortiz, R. P.; Casado, J.; Hernández, V.; Navarrete, J. T. L.; Viruela, P. M.; Ortí, E.; Takimiya, K.; Otsubo, T. *Angew. Chem., Int. Ed.* **2007**, *46*, 9057. (c) Kikuchi, A.; Iwahori, F.; Abe, J. *J. Am. Chem. Soc.* **2004**, *126*, 6526. (d) Porter, W. W., III; Vaid, T. P.; Rheingold, A. L. *J. Am. Chem. Soc.* **2005**, *127*, 16559. (e) Ueda, A.; Nishida, S.; Fukui, K.; Ise, T.; Shiomi, D.; Sato, K.; Takui, T.; Nakasuji, K.; Morita, Y. *Angew. Chem., Int. Ed.* **2010**, *49*, 1678. (f) Koide, T. K.; Furukawa, K.; Shinokubo, H.; Shin, J.-Y.; Kim, K. S.; Kim, D.; Osuka, A. *J. Am. Chem. Soc.* **2010**, *132*, 7246. (g) Kubo, T.; Sakamoto, M.; Akabane, M.; Fujiwara, Y.; Yamamoto, K.; Akita, M.; Inoue, K.; Takui, T.; Nakasuji, K. *Angew. Chem., Int. Ed.* **2004**, *43*, 6474. (h) Konishi, A.; Hiro, Y.; Nakano, M.; Shimizu, A.; Botek, E.; Champagne, B.; Shiomi, D.; Sato, K.; Takui, T.; Matsumoto, K.; Kurata, H.; Kubo, T. *J. Am. Chem. Soc.* **2010**, *132*, 11021. (i) Shimizu, A.; Kubo, T.; Uruichi, M.; Yakushi, K.; Nakano, M.; Shiomi, D.; Sato, K.; Takui, T.; Hirao, Y.; Matsumoto, K.; Kurata, H.; Morita, Y.; Nakasuji, K. *J. Am. Chem. Soc.* **2010**, *132*, 14421. (j) Lambert, C. *Angew. Chem., Int. Ed.* **2011**, *50*, 1756.

(5) (a) Casado, J.; Zgierski, M. Z.; Ewbank, P. C.; Burand, M. W.; Janzen, D. E.; Mann, K. R.; Pappenfus, T. M.; Berlin, A.; Pérez-Inestrosa, E.; Ortiz, R. P.; Navarrete, J. T. L. *J. Am. Chem. Soc.* **2006**, *128*, 10134. (b) Jonkman, H. T.; Kommandeur, J. *Chem. Phys. Lett.* **1972**, *15*, 496.

(6) Zhu, X.; Mitsui, C.; Tsuji, H.; Nakamura, E. *J. Am. Chem. Soc.* **2009**, *131*, 13596.

(7) Kodomari, M.; Satoh, H.; Yoshitomi, S. *J. Org. Chem.* **1988**, *53*, 2093.

(8) Licha, K.; Riefke, B.; Ntziachristos, V.; Becker, A.; Chance, B.; Semmler, W. *Photochem. Photobiol.* **2000**, *72*, 392.

(9) Pappenfus, T. M.; Raff, J.; Hukkanen, E. J.; Burney, J. R.; Casado, J.; Drew, S. M.; Miller, L. L.; Mann, K. R. *J. Org. Chem.* **2002**, *67*, 6015.

(10) Tsuji, H.; Mitsui, C.; Sato, Y.; Nakamura, E. *Heteroatom. Chem.* **2011**, *22*, 316.

(11) (a) Tsuji, H.; Mitsui, C.; Ilies, L.; Sato, Y.; Nakamura, E. *J. Am. Chem. Soc.* **2007**, *129*, 11902. (b) Tsuji, H.; Yokoi, Y.; Mitsui, C.; Ilies, L.; Sato, Y.; Nakamura, E. *Chem.—Asian J.* **2009**, *4*, 655. (c) Ilies, L.; Tsuji, H.; Sato, Y.; Nakamura, E. *J. Am. Chem. Soc.* **2008**, *130*, 4240.

(12) (a) Kamada, K.; Ohta, K.; Kubo, T.; Shimizu, A.; Morita, Y.; Nakasuji, K. *Angew. Chem., Int. Ed.* **2007**, *46*, 3544. (b) Chikamatsu, M.; Mikami, T.; Chisaka, J.; Yoshida, Y.; Aumi, R.; Yase, K.; Shimizu, A.; Kubo, T.; Morita, Y.; Nakasuji, K. *Appl. Phys. Lett.* **2007**, *91*, 043506. (c) Suzuki, Y.; Miyazaki, E.; Takimiya, K. *J. Am. Chem. Soc.* **2010**, *132*, 10453.

(13) (a) Matsuo, Y.; Sato, Y.; Niinomi, T.; Soga, I.; Tanaka, H.; Nakamura, E. *J. Am. Chem. Soc.* **2009**, *131*, 16048. (b) Tsuji, H.; Mitsui, C.; Sato, Y.; Nakamura, E. *Adv. Mater.* **2009**, *21*, 3776.