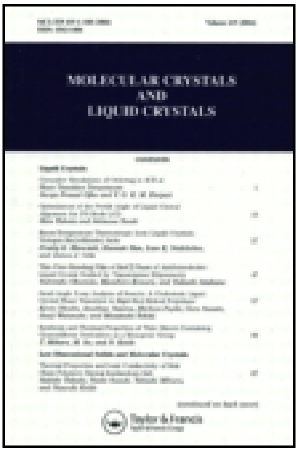

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A Molecular Design towards a Highly Amphoteric and Polar Molecule (HAPM) to Assemble Novel Organic Solid-State Structures

Naoki Sato [a] , Ikuko Kawamoto [a] , Taro Sakuma [a] , Edgar A. Silinsh [b] & Andrejs J. Jurgis [b]

[a] Institute for Chemical Research, Kyoto University, Uji, Kyoto, 611-0011, Japan

[b] Institute of Physical Energetics, Latvian Academy of Sciences, Aizkraukles Street 21, L V-1006, Riga, Latvia

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A Molecular Design towards a Highly Amphoteric and Polar Molecule (HAPM) to Assemble Novel Organic Solid-State Structures

NAOKI SATO[a*], IKUKO KAWAMOTO[a], TARO SAKUMA[a],
EDGAR A. SILINSH[b] and ANDREJS J. JURGIS[b]

[a]Institute for Chemical Research, Kyoto University, Uji, Kyoto 611–0011, Japan and [b]Institute of Physical Energetics, Latvian Academy of Sciences, Aizkraukles Street 21, L V-1006, Riga, Latvia

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To approach a novel molecular assembly with notable electronic properties, a molecular design towards highly amphoteric and polar molecules (HAPMs) as its building blocks is proposed. This design stresses the combination of two different π-molecular segments, electron-donating and accepting ones, particularly with a pseudo-delocalized π-electron system. To examine the suggested contrivance, 2-(4-dicyanomethylenecyclohexa-2,5-dienylidene)-4,5-ethylenedithio-1,3-dithiole **1** was designed and synthesized as a test molecule. Semiempirical MO calculations of **1** and its extended quinonoid analogues indicate a moderately strong intramolecular charge-transfer working in the molecules in the ground state. Moreover, several experimental results of **1**, e.g., its absorption spectra and cyclic voltammograms, imply that most characteristics expected for HAPM are in principle recognized in **1**, though further improvements needed to clear the whole requirements for it.

Keywords: amphoteric molecule; intramolecular charge transfer; intermolecular charge transfer; dipole moment; molecular packing

1. INTRODUCTION

A single compound which works as both an electron donor and an acceptor, as graphite as a typical example, is called an (electronically) amphoteric compound. Although the amphotericity of a molecule should be noteworthy in organic materials science because of its connection with, e.g., a small energy gap between

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[*] Corresponding author.

HOMO and LUMO, only a few studies to produce a highly amphoteric molecule have been reported so far, while a number of synthetic studies have aimed at yielding either a donor or an acceptor.

One approach to the molecular designs of an amphoteric compound is modifying the electron system of a polycyclic aromatic hydrocarbon (PAH) to stabilize its LUMO as well as to destabilize its HOMO, as demonstrated with pentaleno[1,2,3-*cd*:4,5,6-*c'd'*]diphenalene (PDPL, $C_{28}H_{14}$), designed at first as a molecule of the amphoteric multi-stage redox property.[1] PDPL shows the first oxidation potential E_1^{ox} and the first reduction one E_1^{red} to be 0.56 V and –0.43 V, respectively, vs. saturated calomel electrode (SCE), and the difference between these values, $\Delta_1 E = E_1^{ox} - E_1^{red} = 0.99$ V, seems to fall under the smallest value in those obtained so far (cf., $\Delta_1 E = 2.29$ V vs. SCE for dibenzo[*cd*,*lm*]perylene,[1] $C_{26}H_{14}$, a PAH with a molecular structure similar to that of PDPL). However, it could be noted that the control of molecular arrangements in the crystal of a compound like PDPL will be difficult, since they have no characteristic clue for the intermolecular interaction.

In this work, we propose another approach to design a highly amphoteric molecule to have a characteristic electronic structure accessible to the control of the molecular aggregation form using a particular intermolecular interaction, with expecting that unique molecular arrangements to be realized in the crystalline state may lead to novel electronic properties. Our approach aiming at a highly amphoteric compound employs the combination of electron-donating and accepting molecular segments with a pseudo-delocalized electron system, which will cause a high polarity; hence a balance between intramolecular and intermolecular charge-transfer interactions will settle the molecular arrangement as well as physical properties in the crystal.

2. MOLECULAR DESIGN

The present molecular design of a highly amphoteric and polar molecule (HAPM) pays attention to bridging between two molecular segments of π-electron systems in opposite electronic natures: electron-donor (D) and acceptor (A) segments. Besides, a molecular design stressed on the connection of π-electron D and A segments is not unused and has been applied to study characteristic properties of resultant molecules predominantly in the isolated state,[2]-[4] in particular, aiming at the enhancement of optical nonlinearities in organic materials for recent years.[5]-[7] However, the design of HAPM by way of combining D and A segments with the bonding system of a proper electron delocalization, which has been proposed preliminarily,[8] deviates from the conventional designs for those molecules of so-called "push-pull" type. The notable factor for our design consists in considering beforehand associated intermolecular charge-transfer effects, which may lead to notable molecular assemblies, accompanied with a control of intramolecular charge transfer.

To this aspect of the molecular design, the choice of a chemical link between the two segments is influential to the degree of intramolecular charge transfer from D segment to A segment, and such a degree will further affect the magnitude and the form of intermolecular charge transfer in the condensed phase. When a non-conjugated bonding system like a saturated hydrocarbon chain is applied as the link, the two segments are fixed at both ends of the system with almost no intramolecular (through-bond) interaction; such a system can be regarded as so-called "spacer" to arrange those segments as separated at a distance in the crystal.[9]-[11] This kind of molecules might permit a few passive properties such as electric rectification in the solid state as proposed previously by Aviram and Ratner,[9] whereas the desired stacking of D and/or A segments is not necessarily achieved in the crystalline state.[10],[11] On the other hand, when a system of highly efficient π-electron delocalization such as a charge resonance system is employed, the intramolecular (through-bond) charge transfer will rigorously be induced to bring about a nearly zwitterionic charge distribution in the molecule; this could depress a possibility to control molecular arrangements by a balance between the intramolecular and intermolecular charge-transfer interactions in the crystal.

Hence, bonding systems expected to permit a moderately high degree of π-electron delocalization will be adequate to the link between D and A segments. Such a system will keep their electronic natures nearly unchanged, so that intermolecular charge-transfer interactions could further work in the condensed phase. To supplement the idea of the bonding system here, simple energy schemes are shown in Figure 1: the case (a) corresponds to the system in which a state without interaction between D and A is stabilized more than a state with intramolecular charge transfer, and the case (b) in opposition. The link between D and A segments proposed in the present work is expected to realize the case (a), to hold the electronic identities of both segments to a large extent.

Further, to choose not only D and A segments but also the bonding system between them for approaching a HAPM molecule, electronic and steric factors should be considered. The former is required so that each segment should mostly hold a typical electronic nature as D or A and simultaneously the bonding system permits a moderately high degree of π-electron delocalization. The latter is needed so that those segments could be planar to motivate their stacking and/or packing in the crystal and that the whole molecular length may as well be long

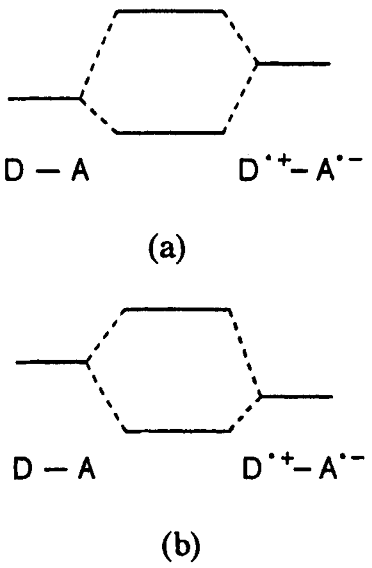


FIGURE 1 Energy schemes for intramolecular charge transfer in a D and A coupled molecule with different stabilities between the non-interacted state and the complete charge-transfer state: (a) the case of the former stabilized more and (b) the opposite case

enough to realize a variety of packing manners owing to possible multiple interactions.

Typical forms of molecular aggregation expected for HAPM are shown in Figure 2: (a) an upright stacking with alternate molecular orientation, (b) an upright stacking with the same orientation, and (c) a slantwise stacking or an engaged one with the same orientation. Among three forms, (a) will be most probable and (b) most unlikely when considering the electrostatic interaction in those crystals, however, (c) may be formed if the electrostatic instability due to gross polarization, derived from molecular dipole moments arranged in the same direction, is suppressed by the intermolecular charge-transfer interaction: a crystal of (c) form could exhibit notable electrical and/or optical properties resulting from the gross polarization. Such a presumable variety in molecular aggregation forms of HAPM may realize a molecular system with, e.g., novel dielectric properties to be controlled by illumination.

With bearing in mind the above factors, several chemical components which seem to be useful to fabricate HAPM have been examined. As a result, in order to produce a test molecule toward HAPM, substituted 1,3-dithiolene groups are selected as D segments with reference to tetrathiafulvalene (TTF) derivatives

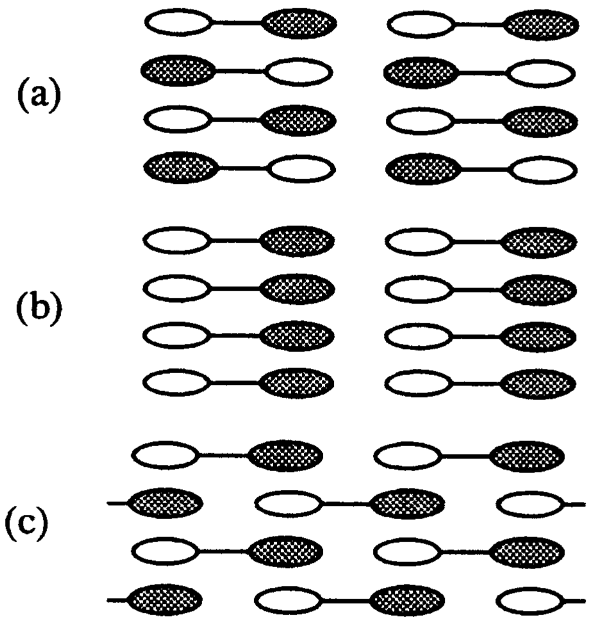
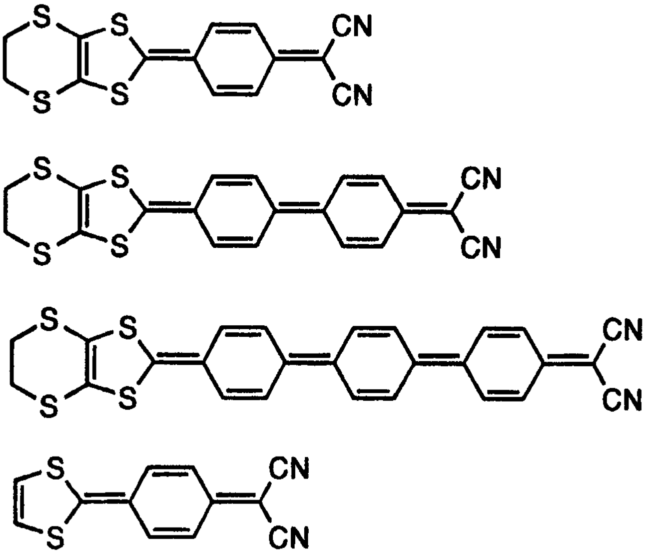


FIGURE 2 Schematics of three kinds of molecular arrangements in the crystalline state supposed for HAPM consisting of D and A segments, shown by open and filled ellipses, respectively, connected with each other: (a) an upright stacking with alternate molecular orientation, (b) an upright sacking with the same orientation, and (c) a slantwise stacking with the same orientation or an engaged stacking with the same orientation

which have given many organic superconductors so far, and a dicyanomethylene group is chosen as an A segment with reference to tetracyanoethylene (TCNE) as a typical electron acceptor. Further, as the bonding system between D and A segments, quinonoids are selected with taking account of a possible contribution of the heterovalent resonance to their electron conjugation, which could be related to a moderately high degree of π-electron delocalization, and the probability of molecular planarity and molecular elongation by repeating themselves. The molecules thus designed are proposed in Figure 3.

The compound **1**, 4,5-ethylenedithio-1,3-dithiolene connected to dicyanomethylene by a single quinonoid unit, is 2-(4-dicyanomethylenecyclohexa-2,5-dienylidene)-4,5-ethylenedithio-1,3-dithiole; the compounds **2** and **3** are its extended analogues with repeated double and triple quinonoid units, that is, diphenoquinoid and triphenoquinoid, respectively. Besides, **1** is regarded as an analogue of the compound **4**, 2-(4-dicyanomethylenecyclohexa-2,5-dienylidene)-1,3-dithiole, which has already been obtained by Gompper, et al.,[2] while



1

2

3

4

FIGURE 3 Structures of the molecules designed for HAPMs. **1**: 2-(4-Dicyanomethylenecyclohexa-2,5-dienylidene)-4,5-ethylenedithio-1,3-dithiole. **2**, **3**: Analogues of **1** with extended quinonoid units. **4**: 2-(4-Dicyanomethylenecyclohexa-2,5-dienylidene)-1,3-dithiole as its simpler analogue

they made this molecule to study intramolecular charge transfer in an isolated state from the viewpoint of physical organic chemistry, but not of organic solid-state chemistry directed to the control of molecular arrangements and charge distributions via molecular condensation, as aimed in this work.

3. MO CALCULATIONS

Prior to the synthesis, MO calculations were carried out to obtain molecular geometries and several molecular parameters of the four compounds in Figure 3. These calculations employed standard HyperChem semiempirical MO methods, that is, AM1 and ZINDO/S approaches.[12],[13] The AM1 method was applied for the geometry optimization, on the other hand, the molecular parameters listed in Table I were calculated with the ZINDO/S method which is parametrized particularly to reproduce optical transitions.[12] For comparison, the ionization energy I_g, the electron affinity A_g and the dipole moment in the ground state μ_{gr} obtained by the AM1 method are also listed in Table I.

TABLE I Ionization energy, electron affinity, dipole moments in the ground and the first excited states, absorption wavelength for the lowest energy transition, oscillator strength and transition dipole moment, calculated for each compound from **1** to **4**

Compound	I_g/eV	A_g/eV	μ_{gr}/D	μ_{ex}/D	λ_{max}/nm	f	M/D
1	7.28	1.61	14.57	20.35	406	1.46	11.9
	7.69	*2.05*	*11.44*				
2	6.53	2.12	20.42	20.90	523	2.86	17.8
	7.28	*2.47*	*15.40*				
3	5.99	2.49	28.03	21.77	653	4.21	24.2
	6.95	*2.77*	*20.64*				
4	7.38	1.66	13.65	16.76	394	1.63	11.7
	7.82	*2.10*	*9.25*				

The molecular geometry was optimized using the AM1 method, and MO calculations carried out using the ZINDO/S approach. I_g and A_g are determined from the orbital energies of HOMO and LUMO, respectively. μ_{gr} and μ_{ex} are obtained to be the same values as their components along the molecular x axis. *Italic* values for I_g, A_g, and μ_{gr}, calculated using the AM1 method, are shown for comparison. 1 eV ≈ 0.1602 aJ and 1 D ≈ 3.3356 × 10^{-30} C m

The geometry optimization calculations of **1** yielded two stable structures with different conformations of the ethylenedithio group as expected. The molecular structure with its staggered conformation (the molecular total energy $E_T = -13231.5$ kJ mol^{-1}) is more stable than that with its eclipsed one ($E_T = -13220.6$ kJ mol^{-1}). The structure with the staggered conformation has, therefore, been applied for further calculations of the compounds from **1** to **3**. The three molecules with the ethylenedithio groups neglected as well as their simplest analogue **4** are completely flat with their symmetry axes coinciding with their long axes defined as the x ones.

Figure 4 shows the bond lengths calculated for **1** in the optimized geometry, which demonstrate expressed quinoid structure regarding the hexagonal carbon ring in the molecule, that is, the lengths for two pairs of C-C single bonds inside the ring (1.445 Å and 1.450 Å) and those for three kinds of C=C double bonds (1.352 Å, 1.371 Å and 1.372 Å) are typical for the bonds in a quinoid structure: e.g., 1.446 Å for each single bond inside the ring and 1.352 Å and 1.374 Å for double bonds inside an outside the ring, respectively, in the case of 7,7,8,8-tetracyano-*p*-quinodimethane (TCNQ).[14] Similar bond length distributions characterize molecular structures also of **2** and **3**.

On the other hand, Figure 5 shows the atomic charge distribution (in the relative units of elementary charge e) over the molecule of **1** calculated with the AM1 method. It is notable that positive charges are distributed mainly over the

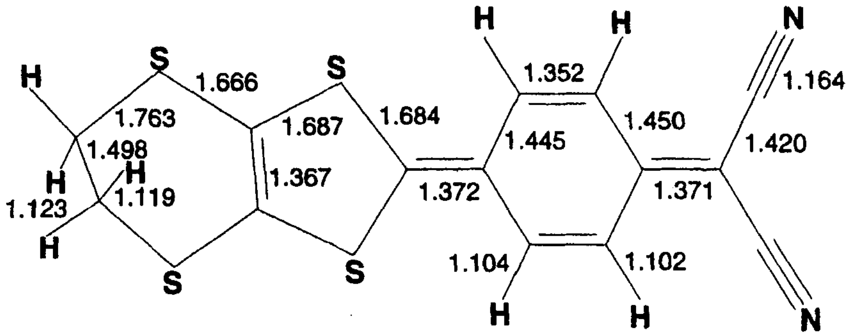


FIGURE 4 Bond lengths (in Å) in a **1** molecule calculated using the AM1 method

ethylenedithiolene and quinonoid fragments of the molecule, which carry +0.17 *e* and +0.10 *e* charges, respectively, while negative charges are located on the small acceptor fragment of dicyanomethylene carrying −0.27 *e* charges. The charge distribution in the molecule is, therefore, considered to be remarkably asymmetric. These results of the molecular geometry and the charge distribution for **1**, which may be regarded to be only apparently contrary to each other, suggest the aimed molecular characteristics based on a moderately high degree of intramolecular charge transfer with preserving original electronic natures of D and A segments to some extent.

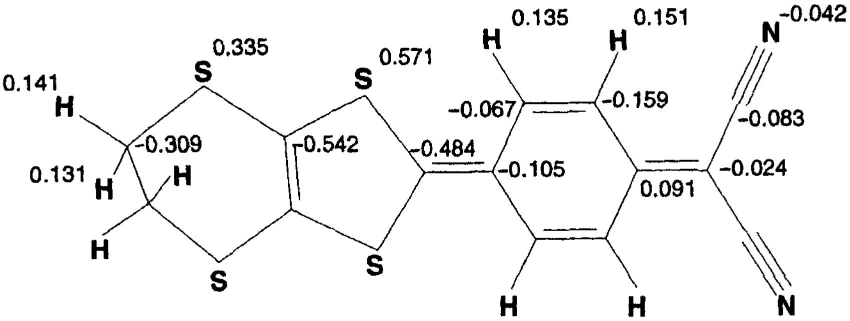


FIGURE 5 Atomic charge distribution in a **1** molecule calculated using the AM1 method. All values are in the relative units of elementary charge *e*

As seen from Table I, the calculated ionization energy of the molecule in the gas phase I_g steadily decreases with increasing molecular length, whereas the electron affinity A_g shows the opposite behavior. As a result, corresponding decrease of the energy gap E_G of these compounds in the solid state can be expected for the increase of the molecular length, similarly as in the case of polyacene series.[15], [16] This predicts significant semiconductive behaviors for the extended analogues of **1** in the crystalline state.

The calculations by the ZINDO/S method have disclosed that the electric dipole moments μ_{gr} and μ_{ex} in the ground and the first excited states, respectively, for **1** and its analogues coincide with their components along the molecular long axis. The μ_{gr} value of each molecule seems to be notably large, and it reaches to 20 and 28 D (1 D ≈ 3.3356×10^{-30} C m) for **2** and **3**, respectively (see Table I). Further, the behavior of the μ_{ex}value could be claimed to be unique. In the case of **1** and **4**, μ_{ex} increases from μ_{gr} considerably through the electronic excitation, which indicates a moderately large charge-transfer (CT) interaction working from D to A segments in those molecules in the ground state, as described above. However, the μ value of **2** does not change practically by the excitation, moreover, μ_{ex} of the longest analogue **3** becomes much smaller than μ_{gr}. These behaviors provide a strong evidence that the electronic transition in **2** and **3** is not of an intramolecular CT nature, and these compounds retain their quinonoid structures with a moderately delocalized electronic structure maintained. This has been confirmed by the electron density maps of the compound **3** at HOMO and LUMO levels, as shown in Figure 6: In LUMO state the electron density cloud is shifted to the opposite direction relative to the dicyanomethylene fragment having the electron accepting nature, which results in the decrease of electric dipole moment in practice.

The transition dipole moment *M* and the corresponding oscillator strength *f* are also remarkably large for all the compounds listed in Table I, so that they can be characterized as probable dye molecules. The value of absorption wavelength for the lowest energy transition λ_{max} shows a notable bathochromic shift from 394 nm to 653 nm with the increase of the molecular length. In the case of **1**, the dipole moment of which increases through the electronic excitation, one may expect positive solvatochromism with increasing polarity of a solvent. On the other hand, such solvatochromism will be negligible for **2**, and, further, even negative solvatochromism could be expected for **3**. Besides, as the color of a compound in the crystalline state is efficiently affected by the manner of molecular packing, a discernible bathochromic shift in absorption spectrum may be expected, if the antiparallel packing of molecular dipoles could be realized in the crystal, as the case shown in Figure 2(a).

Thus, the molecular parameters calculated above suggest that **1** and its extended analogues will possess notable characteristics as HAPM to a large extent, at least as far as the molecular nature is concerned.

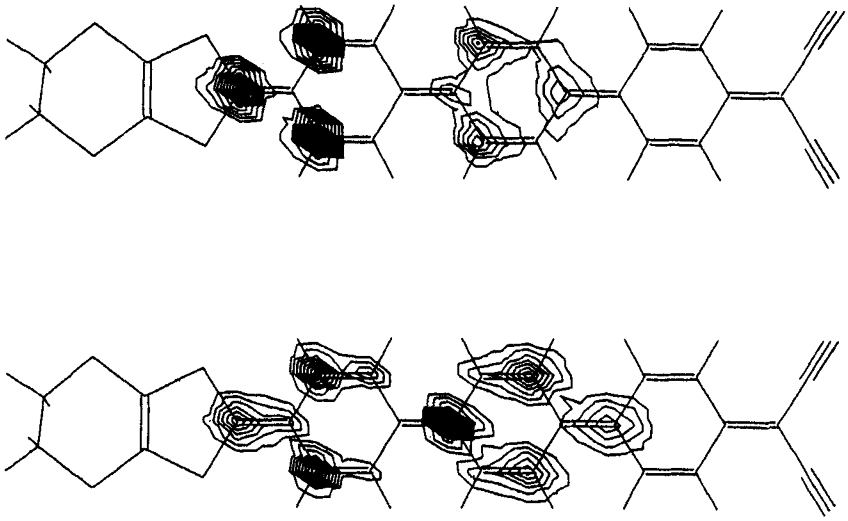
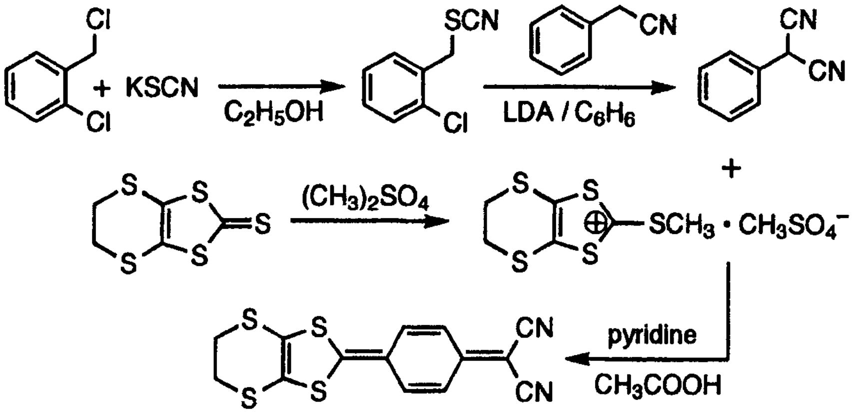


FIGURE 6 Electron density maps of the molecule **3** at LUMO (upper) and HOMO (lower) levels

4. SYNTHESIS OF A TEST MOLECULE

Among the compounds mentioned in Section 2, we have fixed the compound **1** as a test molecule for further studies and tried to produce it to check an essence of the present molecular design. Whereas longer molecules may satisfy more the requirements for HAPM, e.g., the steric requirement above, their syntheses will be more complicated. Thus, the synthetic process of **1** practically used in this work is shown in Scheme 1. The first step to thiocyanate and the second step to phenylmalononitrile were employed with reference to the studies by Schlesinger and Mowry[17] and Davis and Cava,[18] respectively; the yields for the respective steps were 66% and 93%. Both the third step to 2-(methylthio)-1,3-dithiolium and the final step to **1** were employed with reference to those by Gompper et al.,[19], [20] with the overall yield of 35% for these two steps.

It was difficult to purify the final product, dark green fine needles in appearance, by ordinary methods; it is rather insoluble to kinds of organic solvents and is thermally unstable as described below, so that both recrystallization and sublimation were not efficient for purification. Then elemental analysis of **1** ($C_{14}H_8N_2S_4$) after washed by acetic acid, ethanol and ethyl ether in this order gave a fairly good result (calculated: C, 50.57%, H, 2.43%; N, 8.43%; S, 38.57%, found: C, 49.83%, H, 2.39%; N, 8.25%; S, 37.87%). The compound was eventually identified by the high resolution mass spectrometry using a JEOL



SCHEME 1 Synthetic process of **1** employed in the present work, where LDA is abbreviation of lithium diisopropylamide

MStation JMS-700 as follows: the observed value of *m/z*, 331.95671, was in good agreement with the calculated one, 331.957.

5. CHARACTERIZATION OF THE TEST MOLECULE

The obtained compound **1** has been characterized by several methods as described below, to examine if it has the physical and chemical properties expected from the discussion above.

Differential scanning calorimetry (DSC) of **1** was carried out on a DSC-220 of Seiko Instruments. It showed no melting behavior but exothermic one around 300 °C under atmospheric pressure. This indicates that **1** is not thermally stable, so that it seems that vacuum sublimation is not an efficient method to purify this material and also to prepare its single crystal or thin film for investigating solid-state properties.

An electronic absorption spectrum of **1** in a chloroform solution at the concentration of 3.0×10^{-5} mol $l^{-1}$was recorded on a Hitachi U-4000 Spectrophotometer, as shown in Figure 7. The spectrum exhibits the absorption edge at about 720 nm ($h\nu = 1.72$ eV, 1 eV ≈ 0.1602 aJ), an intense absorption band the peak of which is located at 670 nm (1.85 eV) and a small feature at 336 nm (3.69 eV). The band at the longer wavelength comprises vibrational structures, which has been affirmed by an IR absorption spectrum measured on a Nicolet Impact 400 FT-IR Spectrometer. From the molar absorption coefficient for this band, the oscillator strength *f* is evaluated to be 0.75. Although this value is almost a half of $f = 1.46$ calculated for the first singlet transition as shown in Table I, it is still large. Such a large value of *f* can be understood by considering the intramolecular charge transfer to be enhanced by optical excitation; this is consistent with the calculated results of the dipole moments of **1** in the ground and excited states.

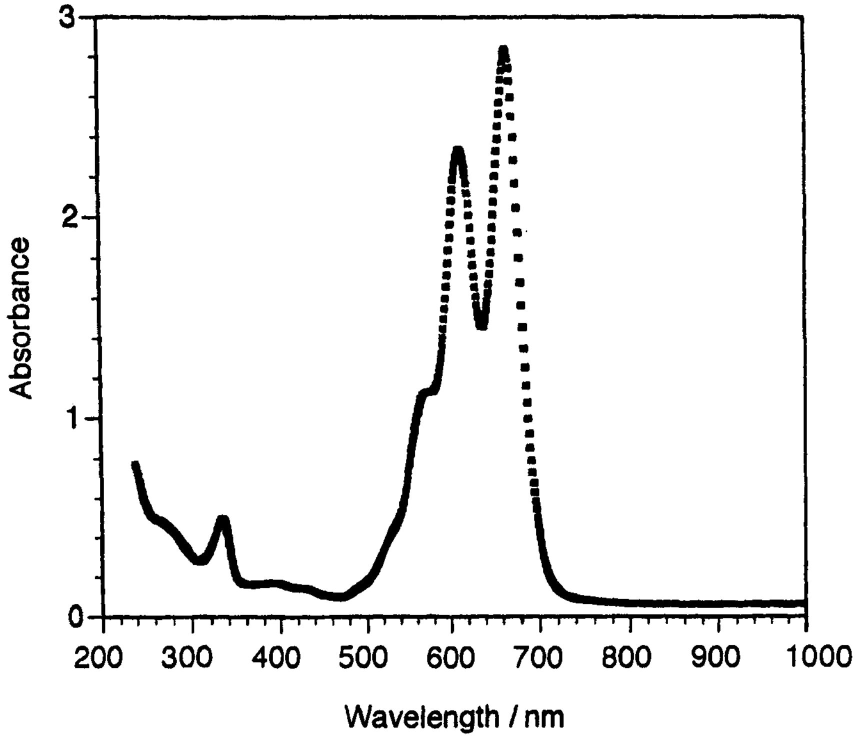


FIGURE 7 Electronic absorption spectrum of **1** in its chloroform solution at the concentration of 3.0×10^{-5} mol l^{-1}

On the other hand, as shown in Table I, the calculated absorption wavelength for the first singlet transition in an isolated **1** molecule is 406 nm ($h\nu \approx 3.05$ eV), which is much smaller than the value observed above, even if a possible influence by solvent is taken into account, where $\lambda = 416$ nm (2.98 eV) has been obtained for molecule surrounded by the solvation shell consisting of fifty eight solvent molecules, using molecular mechanics (atom-atom potential) techniques. Such an inconsistency of the longest absorption wavelength between the calculated and observed results is noted also for other sulfur containing molecules,[21] while the reason is unclear as yet. A thinkable elucidation may be the molecular aggregation effect in solution; molecular aggregates could be formed by a strong electrostatic interaction between polar molecules even at the low concentration of the solution. This may be implied by the lowest absorption wavelength at 600 nm ($h\nu \approx 2.07$ eV) calculated preliminarily for an isolated **1** dimer. Such a strong intermolecular interaction if any will contribute to the molecular aggregation also in the solid state, which could be one of the results derived from the present molecular design of HAPM as discussed in Section 2.

As for the IR spectrum obtained for **1** in a KBr disk, two absorption lines at 2193 and 2167 cm^{-1} are assigned to the stretching mode of cyano groups. Such a spectral splitting of the cyano stretching mode has been observed for **4** (2180 and 2160 cm^{-1}) and its related compounds, and has been discussed with examining wavenumbers of the mode, in terms of structure of a conjugated system connecting D and A segments, i.e., benzoquinoid, naphthoquinoid, anthraquinoid and phenanthrenequinoid units, as well as π bond order of C≡N bonding.[2] In accordance with these consideration, the intramolecular charge-transfer contribution to the electronic structure of **1** seems to be no larger than that in **4**, partly because the bond orders of C≡N bonding are calculated to be almost the same between the two compounds by the PM3 methods. This could support the moderately high degree of electron delocalization (via charge transfer) in the molecule is realized in **1** as expected.

Further, to examine the electrochemical amphotericity of **1**, the measurement of cyclic voltammetry (CV) was carried out on a Yanaco Polarographic Analyzer P-1100 with a typical measurement condition as follows: solvent, supporting electrolyte, a reference electrode and a sweeping voltage rate were 1,2-dichloroethane, 0.1 mol l^{-1} of tetra(*tert*-butyl)ammonium tetrafluoroborate, saturated calomel electrode (SCE) and 100 mV s^{-1}, respectively. Figure 8 shows an observed voltammogram, which gave the first oxidation potential E_1^{ox} and the first reduction potential E_1^{red} to be 0.996 V and −0.619 V vs. SCE, respectively, thus the difference $\Delta_1 E = 1.615$ V.

This value is exactly larger than that of PDPL, 0.99 V, as mentioned in Section 1, however, it is slightly smaller than that (1.65 V[22]) of tetra(methylthio) derivative of bis[1,2,5]thiadiazolo-*p*-quinobis(1,3-dithiole) (BTQBT), known as one of the single-component organic semiconductors with a remarkably narrow energy gap in relation to the molecular amphotericity.[23] Such comparison among $\Delta_1 E$ values indicates that the amphotericity of **1** is fairly high. Accordingly, the present strategy aiming at HAPM is encouraged by the preliminary results on **1** above at least at its molecular level, with bearing in mind that **1** is just a test molecule and molecules like its extended analogues could be still more promising than it.

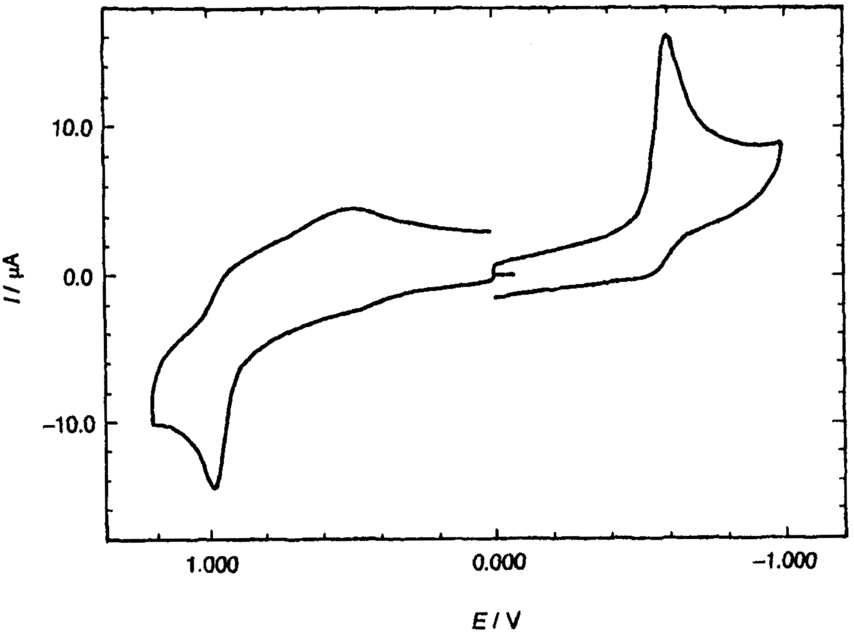


FIGURE 8 A cyclic voltammogram of **1** measured in the following condition: solvent-1,2-dichloroethane, supporting electrolyte-0.1 mol l^{-1} of tetra(*tert*-butyl)ammonium tetrafluoroborate, reference electrode-SCE, and sweeping voltage rate-100 mV s^{-1}

Besides, it has been shown that the $\Delta_1 E$ values of amply large conjugated molecules are empirically equal to (or less by ca. ~10% than) the values of their adiabatic energy gaps in the crystalline state.[24] Such a relation suggests that the adiabatic energy gap could be $E_G{}^a \approx \Delta_1 E \approx 1.6$ eV in the case of **1** crystals. This is much less than $E_G{}^a$ for pentacene (2.47 eV)[15] or phthalocyanines (2.0–2.2 eV).[24] Thus, the extended **1** analogues, **2** and **3**, will show $E_G{}^a$ values still smaller than that of **1**, so that they will be suggested to manifest notable semiconductivity.

6. CONCLUDING REMARKS

In the present work, a molecular design towards highly amphoteric and polar molecules (HAPMs), by way of combining the π-electron donating and accepting segments by the bonding system with a moderately high degree of electron delocalization, has been proposed with aiming at the possible control of molecular arrangements in the condensed phase. After several candidates for each part of an objective molecule have been examined to conform to such a design, an immediate test compound, that is, 2-(4-dicyanomethylenecyclohexa-2,5-dienylidene)-4,5-ethylenedithio- 1,3-dithiole **1**, is offered. Semiempirical MO calculations support largely that **1** has expected characteristics of HAPM, such as a moderate intermolecular charge transfer from the D to A segments, so that **1** has been synthesized and characterized to find a moderately high degree of intramolecular charge transfer working along the molecular long axis from the electronic absorption spectrum and a fairly high amphotericity as comparable as that of BTQBT from the CV measurements.

Thus, the calculated and observed results of **1**, which is employed as a test molecule and does not meet all the requirements for HAPM, could support feasibility of the present molecular design towards HAPM, while molecular arrangements in the crystal have not yet been examined because of the difficulty in preparing crystals and/or thin films of **1** in high qualities due to its low solubility in solution and thermal instability.

In addition, it has recently been reported that extended analogues of the compound **4**, i.e. its extended molecules with two quinonoid units linked, or diphenoquinoid, are synthesized to show their characteristic absorption spectra with the absorption edges at much longer wavelengths: $\lambda \geq 1200$ nm.[25] This kind of compounds, as suggested in the present work, should therefore be noted much more in the field of organic materials science from now on.

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References

[1] K. Nakasuji, K. Yoshida and I. Murata, *J. Am. Chem. Soc.*, **105**, 5136 (1983).

[2] R. Gompper, H.-U. Wagner and E. Kutter, *Chem. Ber.*, **101**, 4123 (1968).

[3] R. Gompper, H.-U. Wagner and E. Kutter, *Chem. Ber.*, **101**, 4144 (1968).

[4] E.g., B. F. Levine, *J. Chem. Phys.*, **63**, 115 (1975).

[5] D. S. Chemla and J. Zyss (eds.), *Nonlinear Optical Properties of Organic Molecules and Crystals* (Academic Press, Orlando, 1987).

[6] J. Zyss (ed.), *Molecular Nonlinear Optics: Materials, Physics, Devices* (Academic Press, Boston, 1993).

[7] C. Mosshard, K. Sutter, Ph. Prêtre, J. Hulliger, M. Flörsheimer, P. Kaatz and P. Günter, in: *Advances in Nonlinear Optics, Vol. 1*, A. F. Garito and F. Kajzar (eds.), (Gordon and Breach, Basel, 1995).

[8] N. Sato and I. Kawamoto, in: *Research report on novel electronic states in molecular conductors*, S. Kagoshima (ed.) (report of scientific research on priority areas No. 253 by the Ministry of Education, Science, Sports and Culture of Japan, 1995), pp. 239–242.

[9] A. Aviram and M. A. Ratner, *Chem. Phys. Lett.*, **29**, 277 (1974).

[10] J. Y. Becker, J. Bernstein, S. Bittner, N. Levi and S. S. Shaik, *J. Am. Chem. Soc.*, **105**, 4468 (1983).

[11] M. P. Le Pillared, A. Robert and C. Garrigou-Lagrange, *Synth. Metals*, **58**, 223 (1993).

[12] *HyperChem Computational Chemistry: Part 1, Practical Guide; Part 2, Theory and Methods*, Hyper Cube, HC 40–00–03–00 (1994).

[13] *HyperChem for Windows: Reference Manual*, Hyper Cube, HC 40–00–02–01 (1994).

[14] R. E. Long, R. A. Sparks and K. Trueblood, *Acta Cryst.*, **18**, 932 (1965).

[15] E.A. Silinsh and V. Cápek, *Organic Molecular Crystals: Interaction, Localization and Transport Phenomena*, (Am. Inst. Phys., New York, 1994), p. 159.

[16] E. A. Silinsh, M. Bouvet and J. Simon, *Mol. Mater.*, **5**, 1 (1995).

[17] A. H. Schlesinger and D. T. Mowry, *J. Am. Chem. Soc.*, **76**, 585 (1954).

[18] W. A. Davis and M. P. Cava, *J. Org. Chem.*, **48**, 2774 (1983).

[19] R. Gompper and E. Kutter, *Chem. Ber.*, **98**, 1365 (1965).

[20] R. Gompper, E. Kutter and H.-U. Wagner, *Angew. Chem.*, **78**, 545 (1966).

[21] E. A. Silinsh, unpublished results.

[22] Y. Yamashita, S. Tanaka, K. Imaeda, H. Inokuchi and M. Sano, *J. Org. Chem.*, **57**, 5517 (1992).

[23] Y. Yamashita, S. Tanaka, K. Imaeda and H. Inokuchi, *Chem. Lett.*, 1213 (1991).

[24] M. Bouvet, E. A. Silinsh and J. Simon, *Mol. Mater.*, **5**, 255 (1995).

[25] S. Inoue, Y. Aso and T. Otsubo, *Chem. Commun.*, 1105 (1997).