Bio-inspired Materials for Electron Donors and Charge-transfer Complex Formation Based on the Imidazopyrazinone Luciferin Core

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The electron-donating properties of 2-phenyl- and 2-methylimidazo[1,2-*a*]pyrazin-3(7*H*)-ones were confirmed by the oxidation potentials. The 1/1 molecular complex from the former and TCNQ was characterized by means of X-ray crystallographic analysis, and the charge-transfer degree was estimated to be 16% from the IR nitrile stretching bands.

There have been several examples of molecule-based electron conducting and/or magnetic materials inspired by ingenious biochemical systems; for example, DNA-mimicking hydrogen-bonded networks are assumed as a promising prescription for crystal engineering.[1,2] However, introduction of sterically bulky periphery (nucleobases etc.) sometimes seems incompatible to desired conducting and/or magnetic properties. Natural organic products have been tuned up for particular biological functions in the evolution history, and such intrinsic functions might be applied to modern technology as well. Recently, cytochrome *c* and chlorophyll *a* have been available for organic light-emitting materials using the electron-transferable nature.[3] We focused on the bioluminescent substrates, luciferins, as straightforward bio-inspired materials. They are readily oxidized with atmospheric oxygen at the initial step of bioluminescence schemes,[4,5] and accordingly we regard them as a potential candidate for electron-donor molecules. The imidazo[1,2-*a*]pyrazin-3(7*H*)-one structure (abbreviated as IP; Scheme 1) is a core of various marine luciferins, which are produced from the crustacea *Cypridina* (*Vargula*)[6] for example. We studied the electron-donating properties of IP derivatives and their ability of charge-transfer (CT) complex formation.

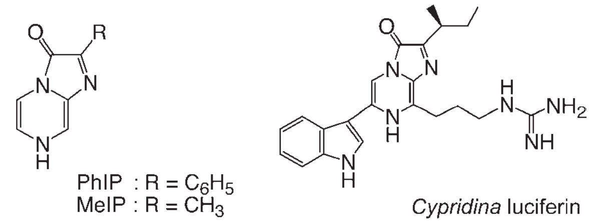
Compounds PhIP and MeIP were prepared according to the reported methods[7–9] and characterized by means of spectroscopic methods.[9] As for MeIP, the hydrochloric salt was prepared by the conventional procedure,[8] and subsequent neutralization of the salt gave the free base MeIP,[9] which was characterized by means of X-ray crystallographic analysis.[10]

We measured cyclic voltammetry (CV) of PhIP and MeIP in acetonitrile but the redox waves were somewhat ambiguous and irreversible even after sufficient de-aeration, possibly owing to decomposition of the cationic form. Measurements in small loops did not improve the irreversible redox curves. The differential pulsed voltammetry (DPV) measurements[11] of PhIP gave a better resolved peak of the first oxidation process at $E_{\mathrm{ox}} = 0.095$ V vs Fc/Fc$^+$, indicating the electron-donating ability of PhIP (Figure 1). Similarly, we confirmed the electron-donating property of MeIP in the DPV measurements. Because of the poor solubility of MeIP, the first oxidation potential was approximately determined to be around −0.05 V. These findings imply that the IP derivatives are good electron donors comparable to ferrocene. An acetonitrile solution containing 1.0 mM of PhIP and TCNQ[12] exhibited new bands at 743 and 842 nm with $\varepsilon = 130$ and 210 dm^3 mol^{-1} cm^{-1}, respectively, which are ascribable to the anion radical form of TCNQ.[13]

The complexation of PhIP with TCNQ in acetonitrile gave brown crystals of a 1/1 molecular complex in 37% yield. X-ray crystallographic analysis revealed that they formed a mixed-stack along the *a* axis (Figure 2).[14] The PhIP portion is practically planar, as found in a neutral form of PhIP,[8,9] and arranged in a parallel manner each other with the TCNQ counter part. Interplane distances between PhIP and TCNQ are 3.30 and 3.37 Å, which are shorter than those of the neutral N-methylated PhIP derivative (3.38 and 3.54 Å)[9] and close to that of graphite (3.35 Å).

Comparison of bond lengths in the TCNQ moiety of PhIP$^{\delta+}$•TCNQ$^{\delta-}$ with those of neutral and monoanionic TCNQ molecules suggested that the CT degree (δ) was small. The bond alternation in a quinoid ring in TCNQ is retained as 1.448 and 1.348 Å on the average for the single and double bonds, respectively, like neutral TCNQ (1.448 and 1.346 Å)[15] rather than monoanionic TCNQ (1.427 and 1.354 Å).[16]

The IR absorption measurement on PhIP•TCNQ revealed the CN stretching band at 2224 cm^{-1}, from which δ was estimated to be ca. 16% by interpolation between those of TCNQ and LiTCNQ measured under the same conditions. From four- and two-probe methods of ac conduction measurements, PhIP•TCNQ was found to be electronically insulating. We can reasonably accept the insulating behavior referring the following re-



Scheme 1.

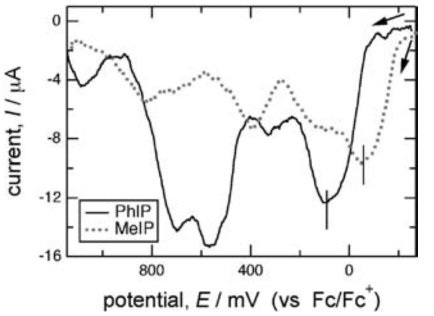


Figure 1. DPV results of PhIP and MeIP in acetonitrile.

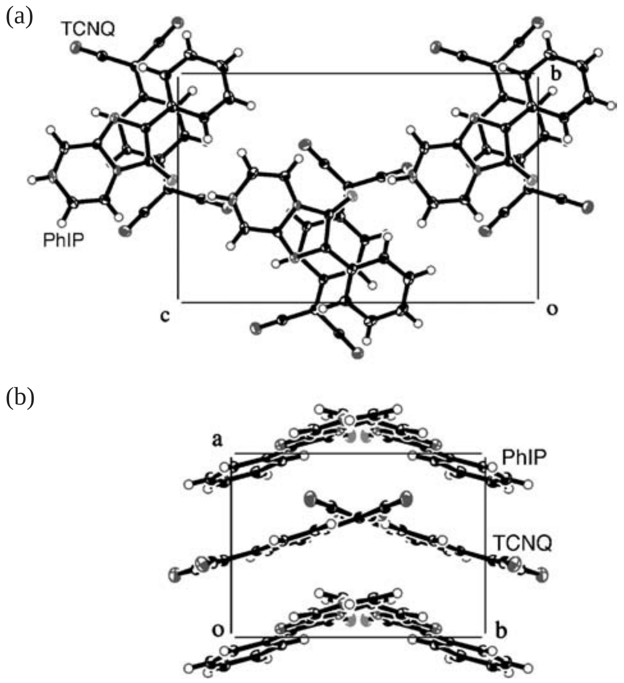


Figure 2. ORTEP drawings of PhIP•TCNQ. (a) A top view and (b) a side view of the mixed-stack columnar structure. Thermal displacement ellipsoids are drawn at the 50% probability level for non-hydrogen atoms.

ports. The first organic "metal" TTF[12]–TCNQ showed a segregated columnar stack with $\delta \approx 0.6$[17] while the insulator phase of BEDT-TTF[12]–TCNQ possessed a mixed-stack columnar structure with $\delta \approx 0.2$.[18] The mixed-stack structure with small δ on the present complex gives rise to low conductivity like the latter case.

In summary, we have revealed the electron-donating properties of the two IP derivatives, PhIP and MeIP, which were characterized by the oxidation potential measurements. The CT degree was confirmed to be substantial but small in PhIP•TCNQ. Though we could not observe conducting behavior from PhIP•TCNQ, complexes with stronger acceptor molecules and ion-radical salts prepared via electrochemical oxidation might improve conducting properties. This work suggests that the natural organic luciferins are versatile electron donors in electronics-oriented materials chemistry.

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10 Selected crystallographic data of MeIP•$(H_2O)_2$: $C_7H_{11}N_3O_3$, triclinic, $P\bar{1}$, $a = 6.556(3)$, $b = 7.786(4)$, $c = 9.680(6)$ Å, $\alpha = 105.91(5)$, $\beta = 104.89(5)$, $\gamma = 105.84(4)^\circ$, $V = 426.8(4)$ Å^3, $Z = 2$, $D_{\text{calcd}} = 1.441\,\text{g cm}^{-3}$, $\mu(\text{Mo K}\alpha) = 0.114\,\text{mm}^{-1}$, $T = 90\,\text{K}$, $R(F)(I > 2\sigma(I)) = 0.053$, and $R_w(F^2)(\text{all data}) = 0.095$ for 1960 unique reflections. Hydrogen atoms were found experimentally and a hydrogen-bonding network was characterized. CCDC reference number 289617.

11 CV and DPV measurements were carried out under the following conditions: 0.01 M solution in acetonitrile, 0.1 M Bu_4NClO_4 as a supporting electrolyte, Pt working and counter electrodes and Ag/Ag^+ reference electrode. In the DPV measurements, the potential was scanned with a rate of +20 mV/s at room temperature and calibrated with the first oxidation potential of ferrocene measured under the same conditions.

12 Abbreviations: TCNQ = 7,7,8,8-tetracyanoquinodimethane; TTF = tetrathiafulvalene; BEDT-TTF = bis(ethylenedithio)-TTF.

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