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Synthesis of the Axially Substituted Titanium Pc-C_{60} Dyad with a Convenient Method

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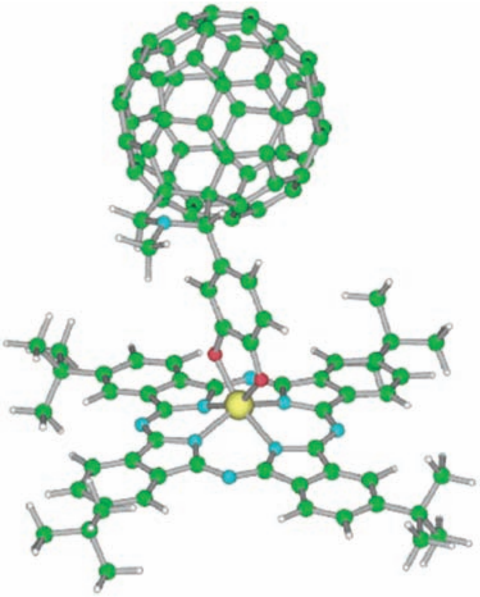
ABSTRACT



We successfully synthesized the axially substituted titanium Pc-C_{60} dyad with a convenient method that improves on the traditional asymmetrical phthalocyanine routine to covalently linked phthalocyanines with other functional molecules. The intramolecular photoinduced process between phthalocyanine donor and fullerene acceptor was preliminarily studied.

Phthalocyanines (Pc's) and fullerenes are well-known building blocks in the area of organic molecular optoelectronic and photonic materials science as a result of their unusual structures and outstanding electric, conducting, and photophysical properties.[1] The combination of the good electron donor and light harvesting characteristics of phthalocyanines

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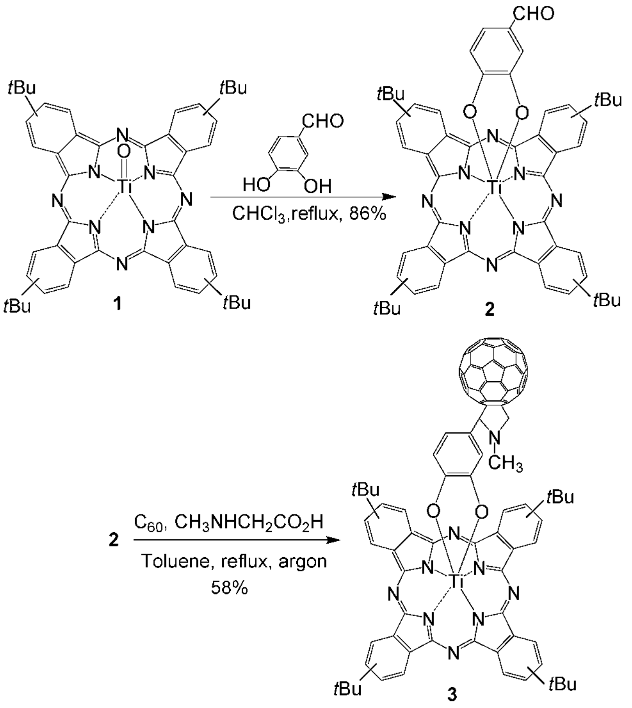
with the excellent electron-accepting properties, larger exciton diffusion length, and low reorganization energy of C_{60} is thus very challenging and will probably become of great importance in the near future.[2,3] As very promising charge generation materials, a tremendous amount of attention has been paid to phthalocyaninato-titanium(IV) oxide (PcTiO) and its derivatives over the past several years.[4,5] The excellent optoelectronic properties and the possibility of preparing flexible films led to their use in photostatic machines or GaAsAl laser printers. The structural and photochemical properties of peripherally substituted 1,(4)- or 2,(3)-phthalocyaninato-titanium(IV) oxides (R_xPcTiO) have also been intensively investigated for a better understanding of the carrier generation process.[6] Fullerenes-based electron donor−acceptor dyads exhibit relatively rapid photoinduced charge separation (CS) and relatively slow charge recombination (CR) as a result of the low reorganization energy of fullerenes.[7] Achieving a long-lived CS state after photoexcitation is the key to realize artificial photosynthesis in supramolecular systems. The first Pc-C_{60} dyad, in which C_{60} was attached peripherally onto the phthalocyanine macrocycle, was synthesized by a Diels−Alder cycloaddition reaction between NiPc diene and C_{60} in 1995.[8] After this, only three new covalently linked Pc-C_{60} derivatives, however, were prepared until now because of the difficulty in the preparation and isolation of asymmetric phthalocyanine precursor used for reaction with C_{60}.[9] In this contribution, we report for the first time an easy route for the synthesis of a new ligand containing C_{60} moiety axially substituted titanium phthalocyanine (Scheme 1), which improves on the traditional asymmetrical phthalocyanine routine to covalently linked phthalocyanines with other functional molecules. Axial substitution in Pc complexes has provoked relevant changes on the electronic structure of the molecule by altering the π-electronic distribution due to the dipole moment of the central metal−axial ligand bond.[10]

Scheme 1



In a typical reaction, the mixture of tBu$_4$PcTiO (**1**) and a 2-fold excess of 3,4-dihydroxybenzaldehyde in chloroform was refluxed under argon for 2 h. After removal of solvent in a vacuum, the crude product was further purified by recrystallization from CH_2Cl_2 by addition of methanol to give green (4-formylcatecholato)-2,(3)-(tetra-*tert*-butylphthalocyaninato)titanium(IV) (**2**) in 86% yield.[11] The driving force of the reaction between tBu$_4$PcTiO and the chelating agent 3, 4-dihydrobenzaldehyde is based on the electrophilic character of titanium(IV) and the nucleophilicity of oxygen atoms in catechol-based derivatives.

The characteristic stretching vibration of Ti═O in the IR spectrum of tBu$_4$PcTiO at 972 cm^{-1} is absent in the IR spectrum of **2** (Figure 1), indicating the replacement of oxygen with the chelating ligand at the central titanium atom in **2**.[11] This formyl phthalocyanine was used to react with C_{60} in the presence of an excess of *N*-methylglycine in refluxing anhydrous toluene to afford **3** in 58% yield. Elemental analysis results of **3** are basically in agreement

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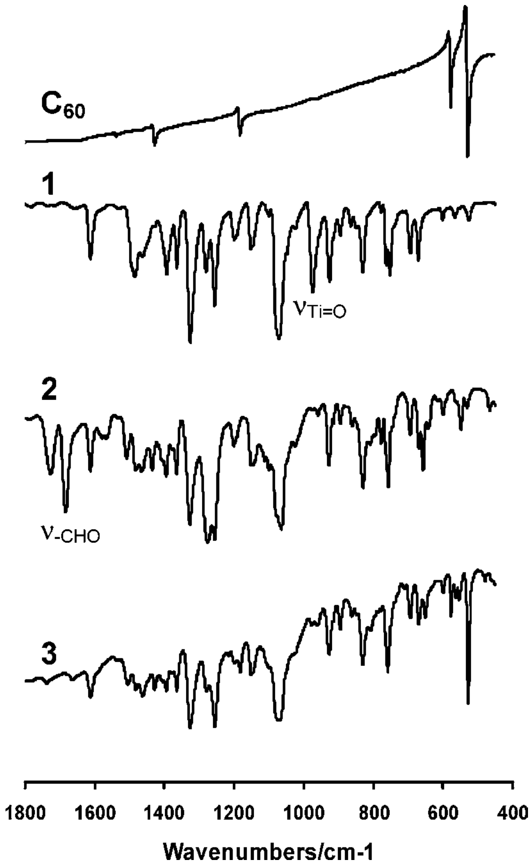
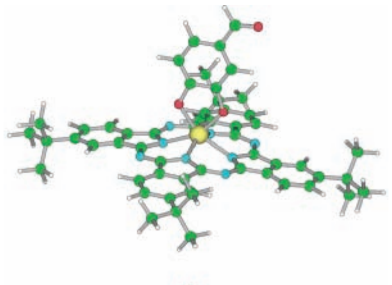


Figure 1. FTIR spectra of C_{60} and compounds **1**−**3**.

with its calculated values. Because of the known difficulties in the combustion of metal phthalocyanines (MPcs) it was usually not possible to obtain satisfactory elemental analysis data for all described compounds.[10,11] The molecular ion peak at *m*/*z* 1669 was detected from the MALDI-TOF mass spectrum of **3** ($C_{117}H_{57}N_9O_2Ti$). The proton NMR pattern of the phthalocyanine rings of **2** and **3** are very similar. The signal for the 36 protons of the *tert*-butyl substituents of the phthalocyanine ring appears at δ 1.7 ppm as an intense and slightly broad signal due to structural isomers of tetrasubstituted phthalocyanines.[10] Axial aromatic groups cause a slightly stronger deshielding of the aromatic protons of phthalocyanine macrocycles, especially of those closer to the heteroaromatic 18 π-electron system, than does the O ligand in **1**. In contrast, the proton signals of the axial ligand in **2** and **3** are considerably shielded by the influence of the large diamagnetic ring-current of the phthalocyanine rings on the protons of their axial ligands. The proton signals of $N-CH_3$ and pyrrolidine H are located at δ =2.1 and 3.4 ppm, respectively.

To get more structural information, optimized structures and molecular orbitals of **2** and **3** were calculated by HF/3-21G level using Gaussian-98 pack. Figure 2 gives the optimized molecular structures of **2** and **3**. Both the HOMO and LUMO of **2** are located on the phthalocyanine macrocycle, while the HOMO and LUMO of **3** are located on the



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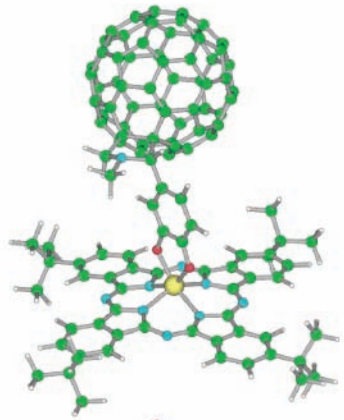

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Figure 2. Optimized structures of compounds **2** and **3**.

phthalocyanine ring as an electron donor, and C_{60} moiety as an electron acceptor, respectively (see Supporting Information). In this case, the charge-separate state of **3** can be presumed to be $(PcTi)^{\bullet +}-C_{60}^{\bullet -}$. The distance between the center of the C_{60} moiety and the Ti atom on the phthalocyanine ring (R_{cc}) is about 10 Å. The HOMO/LUMO values of the phthalocyanines were experimentally estimated by the onset of the redox potentials taking the known reference level for ferrocene, 4.8 eV below the vacuum level,[12] according to the following equation: HOMO/LUMO $= -[E_{onset} - E_{ox(ferrocene)}] - 4.8$ eV. In our electrochemical experiments ferrocene exhibits an oxidation peak with an onset of 0.38 V vs Ag/AgCl. From the onset values of the oxidation potential (E_{ox}) and reduction potential (E_{red}) of **3,** which are 0.416 and −0.728 V vs Ag/AgCl, respectively, the HOMO−LUMO gap of **3** was evaluated to be 1.14 eV. Following the same procedure, one can calculate the HOMO−LUMO gaps of **1** and **2**, which are found to be 1.46 eV for **1** and 1.32 eV for **2**. These findings demonstrated that the presence of electron-withdrawing substituents such as the aldehyde group and [60]fullerene moiety in the catechol-based ligands induces additional electronic effects consisting of a large charge separation and the localization of a partial positive charge on the axial aromatic ring,[11] giving rise to the decrease of the HOMO−LUMO gaps of PcTi complexes.

The axial ligands did not in general affect the linear optical properties of phthalocyanines; the Q- and B-bands in the

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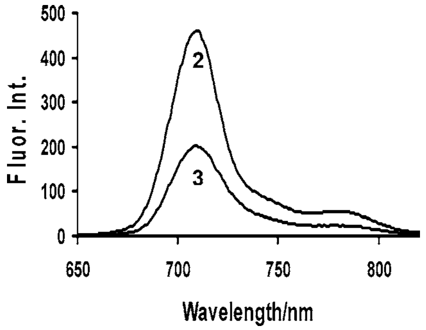

Figure 3. Fluorescence spectra of compounds **2** and **3** in benzonitrile (1×10^{-6} M); $\lambda_{ex} = 420$ nm.

UV−vis spectra are shifted only slightly by a few nanometers on exchangingthe axial ligands on the metal.[10,11] Compared to the UV−vis absorption spectrum of *t*Bu$_4$PcTiO, the Q-bands of **2** and **3** are slightly shifted to the red as a result of the electron-withdrawing aldehyde and C_{60} substitutents. The weak absorption band at $\lambda = 430$ nm typically assigned to the [6,6]closed monosubstituted fullerene derivative was observed in the UV−vis absorption spectrum of **3**. Upon excitation with a laser light of 420 nm, all compounds display a Stokes shift of the emission peak with respect to the location of the Q-band absorption in deaerated benzonitrile. Small Stokes shifts imply that the structure change between the ground state and the excited singlet state is very small.

Fluorescence spectra of **2** and **3** were measured under the same experimental conditions, as shown in Figure 3. Although the fluorescence peaks of C_{60} moiety appear in the same region, the fluorescence intensity of the C_{60} moiety is usually quite low.[7] It's thus reasonable that the fluorescence of **3** was mostly from the PcTi moiety. In polar solvents such as benzonitrile, THF, and others, a considerably quenching of the fluorescence intensity was found. This observation suggests a quenching of the singlet excited PcTi by the appended C_{60} moiety. The driving force for the charge-separation process ($-\Delta G_{CS}$) was calculated according to equation[13]

$$\Delta G_{CS} = E_{1/2}\left(\frac{\mathrm{PcTi}^{\bullet +}}{\mathrm{PcTi}}\right) - E_{1/2}\left(\frac{C_{60}}{C_{60}{}^{\bullet -}}\right) - \Delta E_{0-0} - \Delta G_s \quad (1)$$

where ΔE_{0-0} refers to the energy of the 0−0 transition energy gap between the lowest excited state and the ground state of C_{60} or PcTi (1.75 eV for both $^1C_{60}{}^*$ and $^1\mathrm{PcTi}^*$). ΔG_s represents the solvation energy that calculated as 0.06 eV in benzonitrile employing the center−center distance (R_{cc} = 10 Å). The ΔG_{CS} value for **3** was evaluated to be −0.67 eV, indicating that the energy level of the radical ion pair, $\mathrm{PcTi}^{\bullet +}$−$C_{60}{}^{\bullet -}$, is located lower than the singlet excited state of C_{60} and PcTi but higher than the ground state. The negative ΔG_{CS} value demonstrates that the charge-separation process via $^1\mathrm{PcTi}^*$ and/or $^1C_{60}{}^*$ are exothermic and favorable in benzonitrile. The fluorescence quenching of **3** might thus be associated with the intramolecular charge-separation process. The charge-separation process was initially confirmed by applying nanosecond laser flash photolysis. Upon the excitation of 532 nm laser light, which excites the C_{60} moiety predominately, the transient absorption spectrum of **3** was obtained in benzonitrile (Figure 4). The quick raise-decay at 790 and 1020 nm were observed. These two absorption bands might be assigned to the formation of $\mathrm{PcTi}^{\bullet +}$ and $C_{60}{}^{\bullet -}$, respectively.

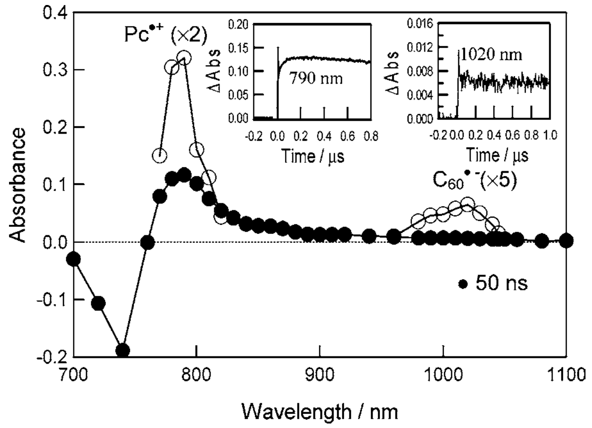

Figure 4. Transient absorption spectra of **3** (0.1 mM) in Ar-saturated benzonitrile (λ_{ex} = 532 nm). Inset: absorption−time profiles at 1020 and 790 nm.

In summary, the axially substituted titanium Pc-C_{60} dyad (**3**) has been prepared by using a convenient method that improves on the traditional asymmetrical phthalocyanine routine to covalently linked Pc's with other functional molecules. The HOMO−LUMO gaps of compounds decrease gradually, from 1.46 eV for **1** to 1.32 eV for **2** to 1.14 eV for **3.** Compared to the UV−vis absorption spectrum of *t*Bu$_4$PcTiO, the Q-bands of **2** and **3** are slightly moved to the longer wavelength. Intramolecular charge separation in **3** was supported by the negative free-energy change calculated by the electrochemical data, and by the nanosecond transient absorption experiments. Further studies on the optoelectronic properties and nonlinear optical properties of **3** are currently ongoing.

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Supporting Information Available: General synthetic procedures and structural characterization data for compounds **1**−**3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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