## Supporting Information (OL050281L)

# Synthesis of the axially substituted titanium Pc-C<sub>60</sub> dyad with a convenient method

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## **Experimental section**

## 1. General

The operations for synthesis prior to the termination reaction were carried out under purified argon. [60]Fullerene (99.5%) was purchased from Aldrich and used without further purification. Solvents were purified, dried and distilled under dry nitrogen. UV/Vis absorption spectra were recorded on a JASCO V-530 UV/Vis spectrophotometer; Photoluminescence spectra were measured by Shimadzu spectrofluorophotometer; <sup>1</sup>H-NMR spectra were performed on a JEOL LAMBDA 400 (<sup>1</sup>H: 250.131 MHz; CDCl<sub>3</sub> as solvent); Analytical thin layer chromatography (TLC) was performed using aluminium coated Merck Kiesegel 60 254 plates. FTIR spectra were measured on Bruker IFS 48; MALDI-TOF-MS measurements were performed on a Bruker REFLEX III-S (preparation method of sample: the samples were dissolved in dry THF, then mixed 1:1 (0.8  $\mu$ l each) with a methanol solution of  $\alpha$ -cyano-4-hydroxycinnamic acid as matrix); Elemental Aanalyses: Carlo-Erba Elemental Analyser 1104, 1106. Due to the known difficulties in the combustion of phthalocyanines it was not possible to obtain satisfactory elemental analysis data for all described compounds. Cyclic voltammetric data were obtained on a BAS CV-50W voltammetric analyzer with a scan rate of 100 mV/s. Glassy carbon, a platinum wire and Ag/Ag<sup>+</sup> were used as the working, counter and reference electrodes, respectively. Tetrabutylammonium hexafluorophosphate (TBAH, 0.1 M) in dry acetonitrile was used as the electrolyte. Before scan the solution was saturated with nitrogen. HOMO/LUMO values of the phthalocyanines were estimated by the onset of the redox potentials taking the known reference level for ferrocene, 4.8 eV below the vacuum level. In our experiments ferrocene exhibits an oxidation peak with an onset of 0.38 V vs Ag/AgCl. In this case, their values can be calculated by the equation: HOMO/LUMO = -Eonset + 0.38 eV - 4.8 eV.

# 2. Preparation of the samples

Synthesis of 2,(3)-(Tetra-tert-butylphthalocyaninato)titanium(IV) Oxide

(tBu<sub>4</sub>PcTiO)



### **Compound 1**

This product, a blue microcrystalline powder, was provided by Prof. Dr. Mutsumi Kimura (see Acknowledgement section). The spectral data as follows:

UV/Vis (CHCl<sub>3</sub>):  $\lambda$ max = 699, 630, 347 nm; PL (CHCl<sub>3</sub>):  $\lambda$ max<sup>fluo.</sup> =717 nm ( $\lambda$ <sub>ex</sub> =630 nm); 1H-NMR (CDCl<sub>3</sub>):  $\delta$ /ppm =1.95-1.89(s, 36H, CH<sub>3</sub>); 8.39-8.29(m, 4H, H-1); 9.23-9.12(m, 8H, H-2,2'); IR(KBr): 2956s, 2905s, 2363m, 2338m, 1734w, 1718s, 1613m, 1484m, 1393m, 1364m, 1326s, 1280m, 1256ms, 1200w, 1152m, 1072s, 974m ( $\nu$ <sub>Ti=O</sub>), 925m, 894w, 864vw, 830m, 757vw, 762m, 751m, 694m, 670m, 601w, 566w, 525w cm<sup>-1</sup>;

EA: C48H48N8OTi (800.84): cacld. C 71.99, H 6.04, N 13.99; found C71.61. 6.27, 13.62; MALDI-TOF-MS: m/z = 800.62 (M<sup>+</sup>)

Synthesis of (4-Formylcatecholato)-2,(3)-(tetra-*tert*-butylphthalocyaninato) titanium (IV)



## **Compound 2**

*t*Bu<sub>4</sub>PcTiO (200 mg, 0.2497 mmol) and 3,4-dihydroxybenzaldehyde (0.724 mmol) were dissolved in 150 ml of anhydrous CHCl<sub>3</sub> and heated for 1.5 h under reflux under N<sub>2</sub> atmosphere. After cooling to room temperature the solvent was evaporated and the residue was recrystallized from dichloromethane by addition of methanol to yield green solid powder, which was dried at 70<sup>o</sup>C under valuum for several hours. Yield: 198 mg (86%); green powder, m.p.> 300<sup>o</sup>C. UV/Vis (benzonitrile):  $\lambda$ max = 702, 634, 352 nm; PL (benzonitrile):  $\lambda$ max<sup>fluo.</sup> =710 nm ( $\lambda$ <sub>ex</sub> =420 nm); <sup>1</sup>H-NMR (CDCl<sub>3</sub>):  $\delta$ /ppm =1.99-1.88(s, 36H, CH<sub>3</sub>); 4.39-4.18(d, 1H, H- $\beta$ ). 4.75-4.56 (d, 1H, H- $\chi$ ), 6.02-5.85(s, 1H, H- $\beta$ '), 8.45-8.28 (m, 4H, H-1); 8.78-8.66(s, 1H, CHO), 9.55-9.01(m, 8H, H-2,2'); IR(KBr): 2961s, 2363vs, 2338s, 1727ms, 1684s(v<sub>CHO</sub>), 1613m, 1558w, 1567w, 1509m, 1483m, 1466m, 1435m, 1395m, 1365m, 1327s, 1276vs, 1256s, 1200m, 1146m, 1064s, 927ms, 895m, 860m, 829ms, 776m, 756ms, 693m, 669ms, 641m, 599m, 548m, 530w, 465w cm<sup>-1</sup>; EA: C<sub>55</sub>H<sub>52</sub>N<sub>8</sub>O<sub>3</sub>Ti (920.36): calcd. C71.73, H 5.69, N 12.17; found: C 70.12, H 5.23; N 11.67; MALDI-TOF-MS: *m/z* =920.50(M<sup>+</sup>)

Synthesis of  $[4-(N-methylfullereno-C_{60}-(1,9-c)pyrrolidine)catecholato]-2,(3)-tetra$ butylphthalocyaninato)-titanium(IV)



#### **Compound 3**

A stirred mixture of **2**(140 mg, 0.152 mmol), C<sub>60</sub> (109.5 mg, 0.152 mmol) and Nmethylglycine (13.6 mg, 0.152 mmol) in dry toluene (160 ml) was refluxed under argon for 48 h. After chromatography over silica gel using toluene/ethyl acetate (v/v: 95:5) as eluting solvents, the obtained solid product was further subject to recrystalization from CH<sub>2</sub>Cl<sub>2</sub>/MeOH to afford 253.8 mg of the blackish green compound **3** in 57.7% yield. UV/Vis (benzonitrile):  $\lambda$ max = 704, 634, 430, 332 nm; PL (benzonitrile):  $\lambda$ max<sup>fluo.</sup> =709 nm ( $\lambda_{ex}$  = 420 nm); <sup>1</sup>H-NMR (CDCl<sub>3</sub>): δ/ppm =1.77-1.72(s, 36H, CH<sub>3</sub>); 3.42 (br, 3H, pyrrolidine H), 2.10(s, 3H, N-CH<sub>3</sub>), 4.41-4.38 (d, 1H, H-β). 4.78-4.72 (d, 1H, H- $\chi$ ), 7.71(s, 1H, H-β'), 8.34-8.27 (m, 4H, H-1); 9.57-9.34(m, 8H, H-2,2'); IR(KBr): 2960s, 2364vs, 2336s, 1727ms, 1666w, 1611m, 1556w, 1564w, 1506m, 1483m, 1463m, 1428w, 1394w, 1364m, 1325s, 1274m, 1255s, 1200w, 1182m, 1151m, 1071vs, 960w, 926ms, 895m, 861w, 830ms, 775w, 758s, 694m, 669m, 650m, 599w, 576m, 562m, 553m, 527s, 478w cm<sup>-1</sup>; EA: C<sub>117</sub>H<sub>57</sub>N<sub>9</sub>O<sub>2</sub>Ti (1668.63 g/mol): calcd. C84.22, H 3.44, N7.55; found: C82.02, H 3.63; N6.01; MALDI-TOF-MS: *m/z* =1669.27(M<sup>+</sup>), 949.3(M-C<sub>60</sub>)<sup>+</sup>.



Figure 1. The HOMO/LUMOs of compounds 2 and 3 calculated by HF/3-21G level using Gaussian-98 pack.



Figure 2. MALDI-TOF mass spectrum of compound 3.