Electronic Supplementary Material (ESI) for Chemical Communications

Supporting Information

A High Voltage Organic-Inorganic Hybrid Photovoltaic Cell Sensitized with Metal-ligand Interfacial Complexes

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Experimental details

Device fabrication: The organic-inorganic hybrid photovoltaic cells were prepered using the following procedure. Transparent conducting oxide (TCO) glass (10 Ω/sq, GEOMATEC Co., Ltd.) was cleaned ultarasonically in acetone, isopropanol, and ultra-pure water sequentially for 10 min each. The TCO glass was pre-treated with a 0.05 mM aqueous $TiCl_4$ at 70 °C for 30 min. After being dried by N_2-gas and heated at 150 °C, mesoporous TiO_2 films (1 μm) were screen printed by using a commercial TiO_2 screen printing paste (PST-18 NR, JGC Catalysts and Chemicals Ltd.). Sintered electrodes were immersed in ethanol solution of 1-Amino-4-hydroxyanthraquinone (AQ) (1.0 mM, Tokyo Chemical Industry Co., Ltd.) and kept at 75 °C for 1 hours. As hole-transporting layers (100 nm), perylene (Tokyo Chemical Industry Co., Ltd.) was sequentially stacked by the vapor deposition method under a pressure of about 2.0×10^{-5} Pa. Finally, Au top electrodes (100 nm) were thamally evapolated on the perylene films.

Measurements: The film thickness was measured by the stylus surface profiling system (Dektak 150, ULVAC, Inc.). AFM images were obtained on a SPM-9700 (Shimadzu corporation). Electronic absorption spectra were measured with a UV-1800 spectrophotometer (Shimadzu corporation). Infrared and Raman spectra were recorded with IRPrestige21/AIM8800 (Shimadzu corporation) and Nanofinder (Tokyo Instruments Inc.), respectively. Thin film structures of the perylene film were characterized by X-ray diffraction using CuKα radiation (BRUKER D8 DISCOVER/Hybrid). Photocurrent density–voltage (*J–V*) curves were measured by a computer-controlled digital source meter (Keithley 2400) under iradiation by a PEC-L01 solar simulator (AM 1.5 G, 100 mW/cm^2, Peccell Technologies, Inc.). Incident photon-to-current conversion efficiency (IPCE) was recorded with PEC-S20 action spectrum measurement setup (Peccell Technologies, Inc.). The ionization potential in the air was estimated by the photoemission yield spectrometer (AC-3, RIKEN KEIKI CO., LTD.).

Density functional theory (DFT) calculation: All the calculations were carried out with three-parameterized Becke-Lee-Yang-Parr (Restricted B3LYP) hybrid exchange-correlation functional. The 6-31g (d, p) basis set was used for C, H, N, and O, and 6-31g ++(3d, 3p) for Ti.

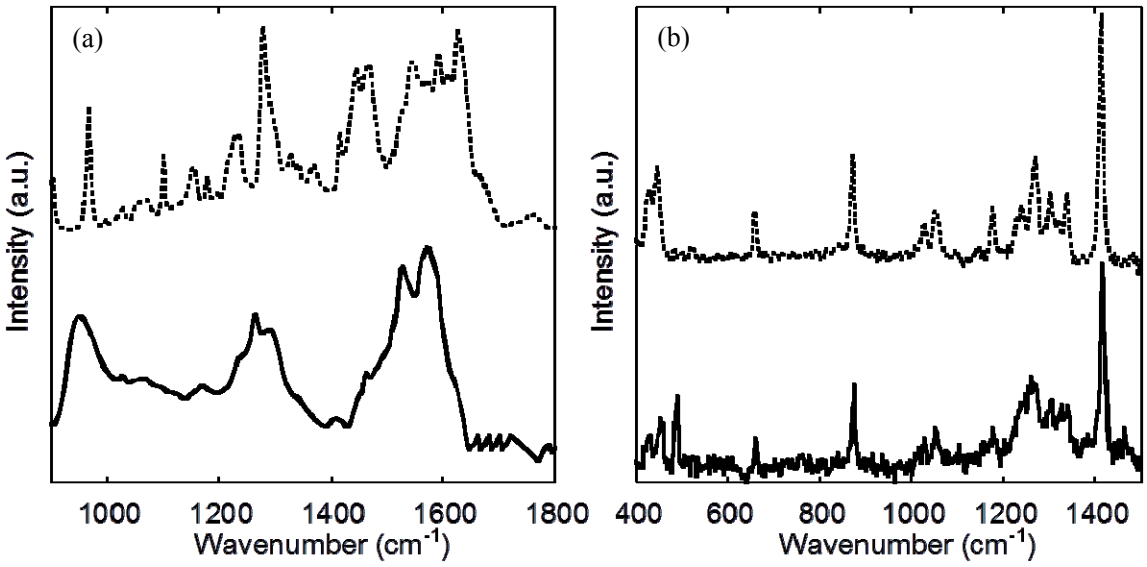

Figure S1. FT-IR (a) and Raman (b) spectra of AQ coordinated on TiO_2 (solid line) and AQ in the solid film (dotted line). In the IR spectra, AQ in the solid film shows the hydroxyl group vibration of the ρ(OH) mode at ~1450 cm^{-1}, while the corresponding one of AQ coordinated on TiO_2 disappears. The Raman spectra also show the C-O(H) modes of AQ in the 400-500 cm^{-1}, which are shifted to higher energy by coordination with Ti^{4+}. There is no change of the NH mode of AQ at 657 cm^{-1}, indicating that the NH_3 group of AQ is not concerned in the coordination bond with Ti^{4+}.

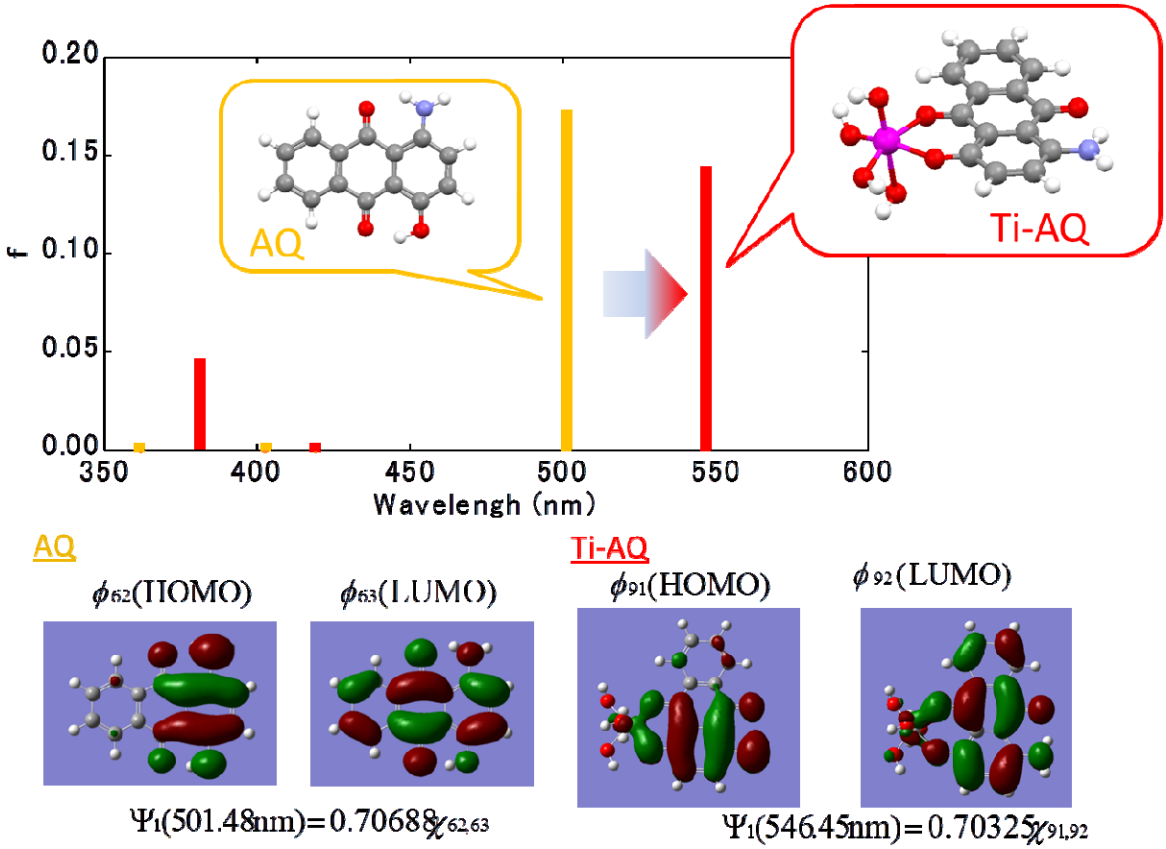

Figure S2. Molecular orbitals and the main transitions of AQ and Ti-AQ calculated with TD-DFT (Restricted B3LYP 6-31g (d, p), 6-31g ++(3d, 3p)).

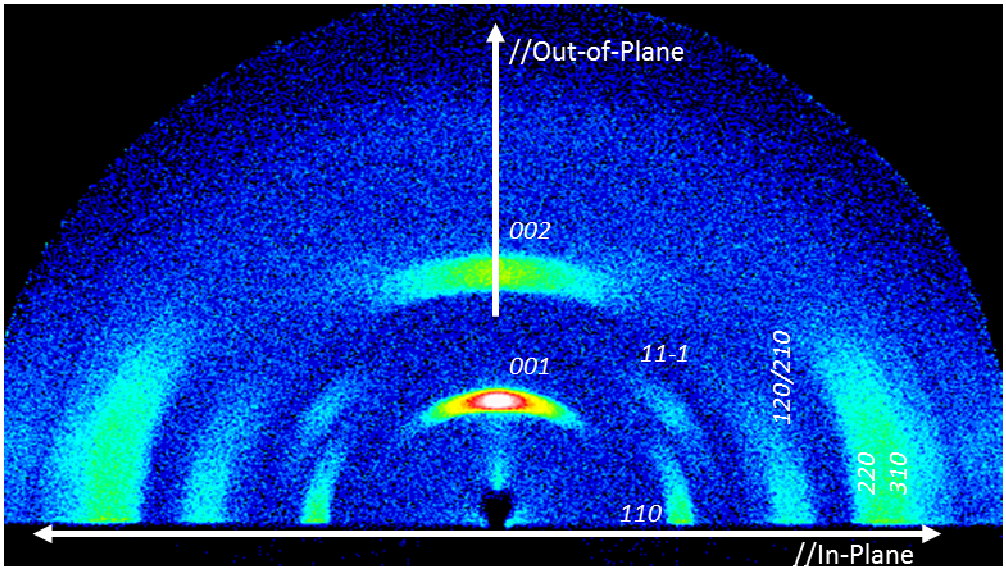

Figure S3. 2D X-ray diffraction profile of perylene in crystal phase, together with assignments of the Bragg reflections.

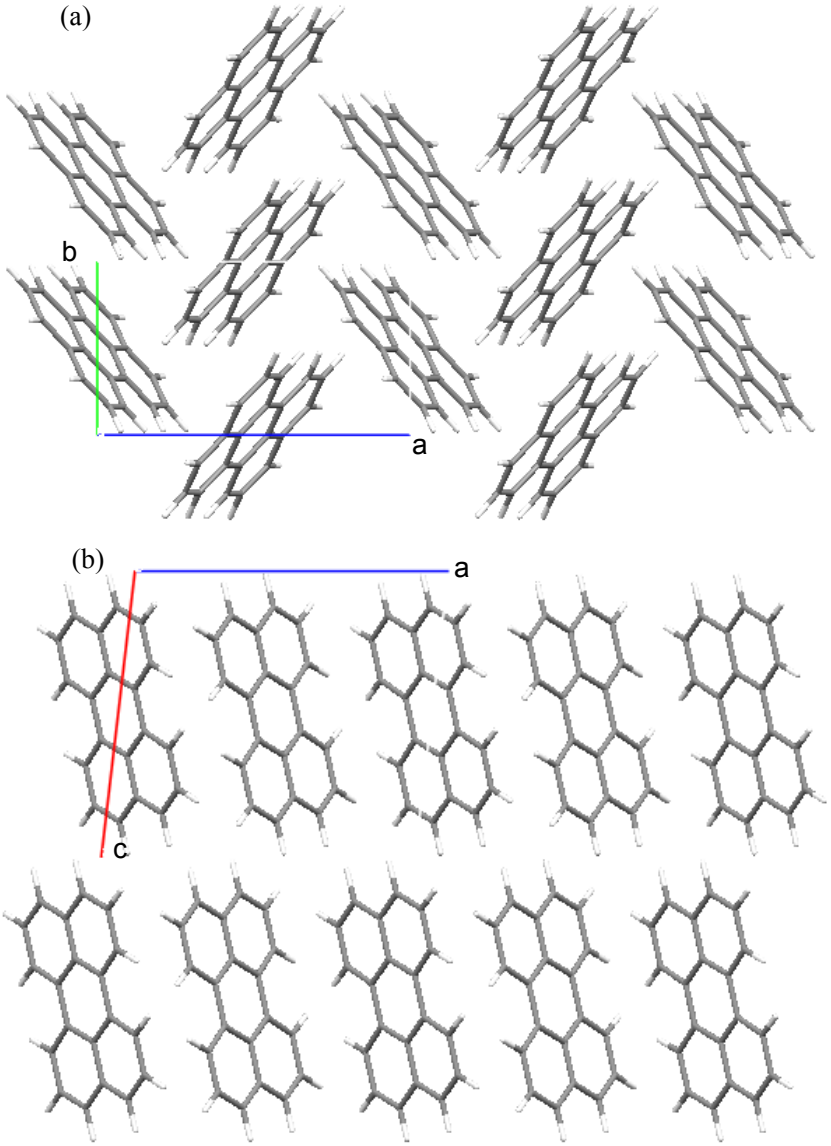

Figure S4. Projection views on (a) ab and (b) ac planes of *β*-form perylene crystal.

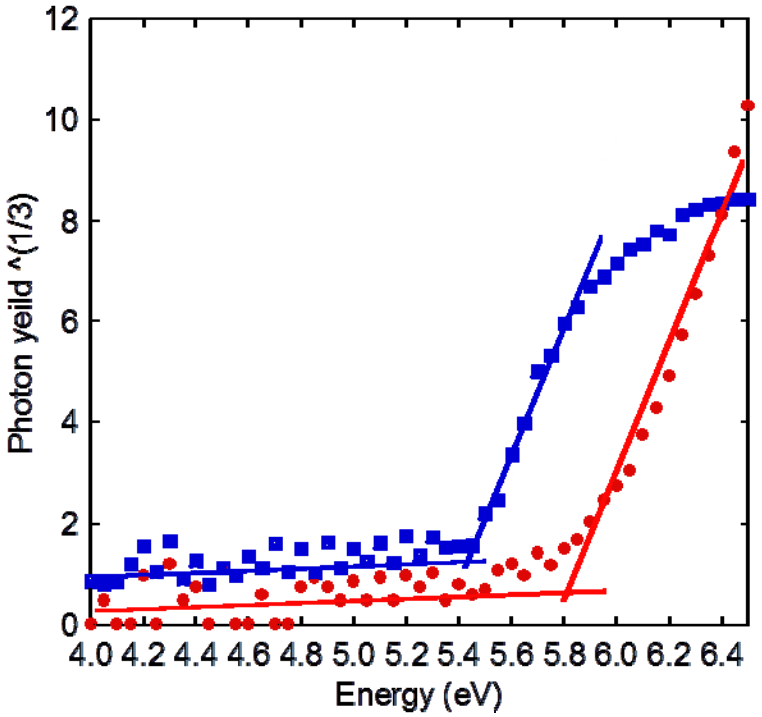

Figure S5. Photoemission yield spectra of Ti-AQ (red) and Perylene (blue) films in the air.

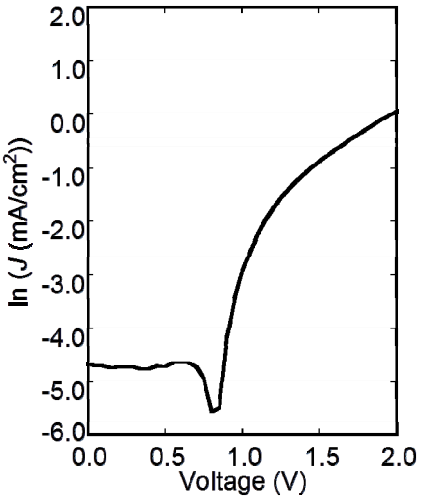

Figure S6. The dark *J–V* characteristics of a photovoltaic cell TCO/TiO_2/Ti-AQ/ Perylene(crystal)/Au (Cell3).