Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information

Visible Light Absorption and Photoelectrochemical Activity of Colorless Molecular 1,3-Bis(dicyanomethylidene)indane (BDMI) by Surface Complexation on TiO_2

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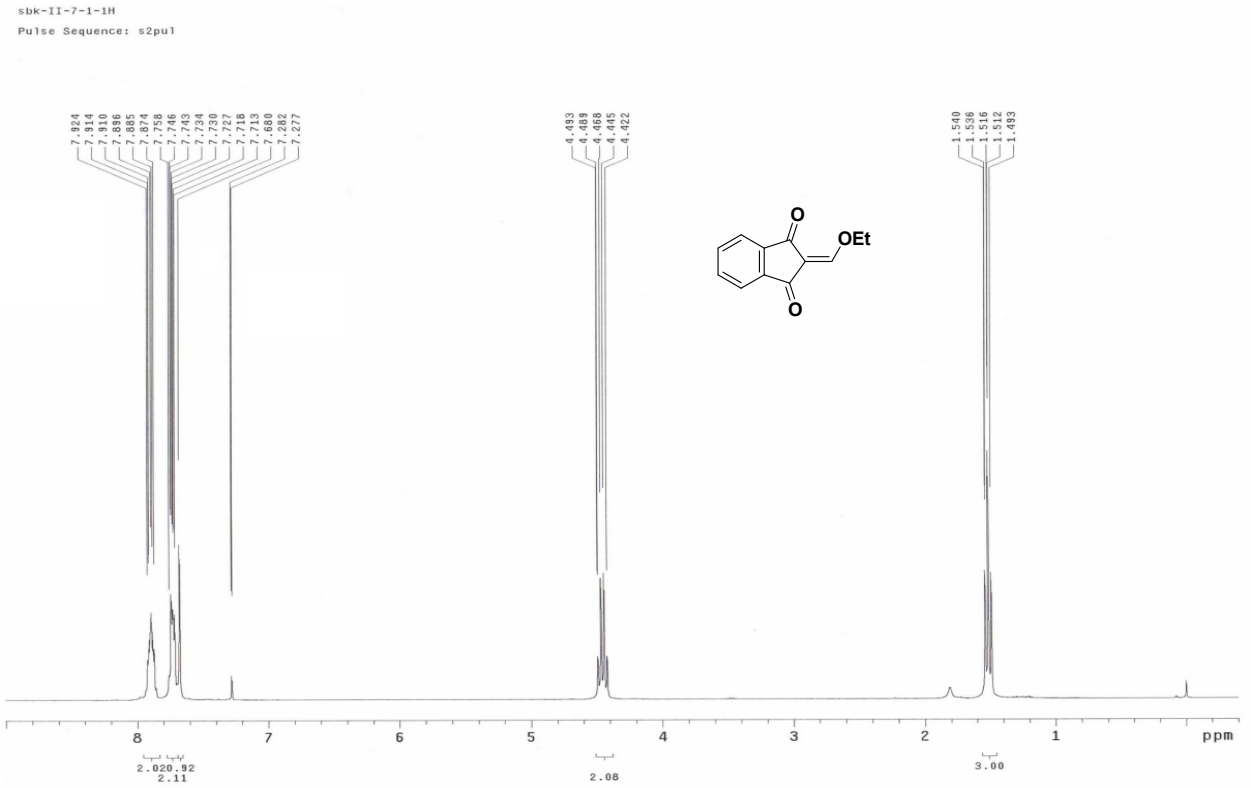
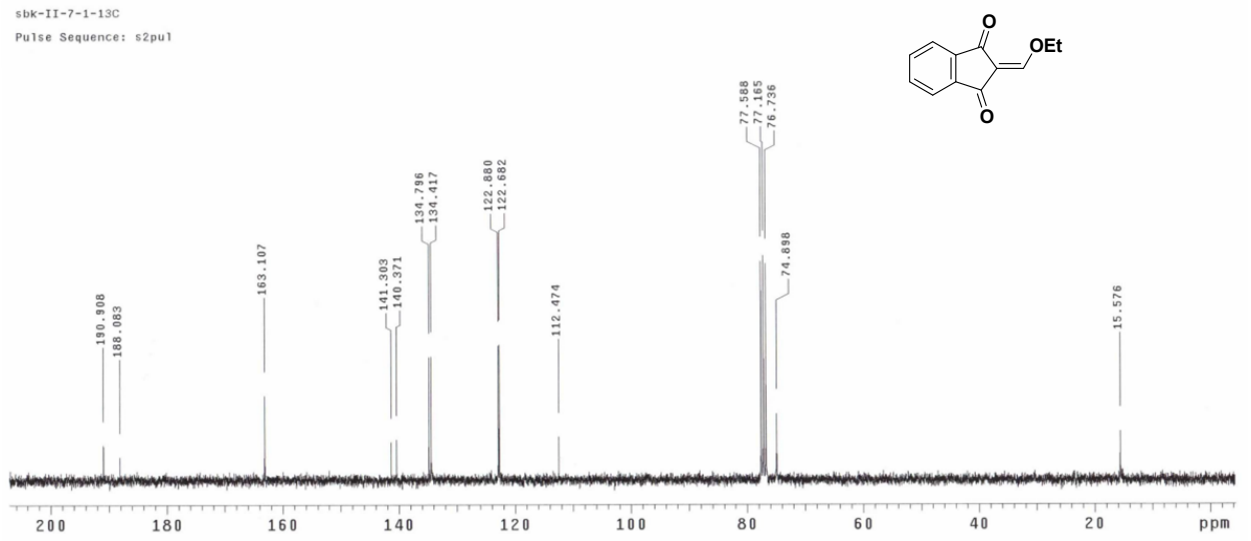
Contents

I. NMR Data

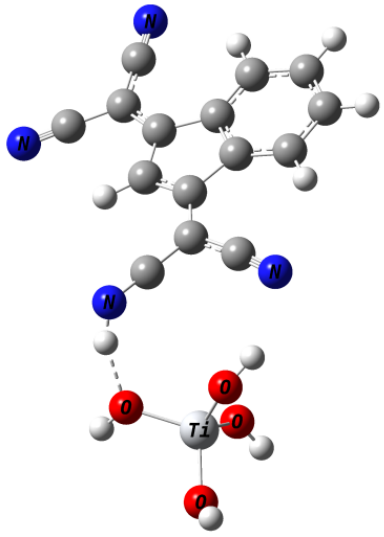
i) ^{1}H NMR of **IDN-OEt**



ii) ^{13}C NMR of **IDN-OEt**



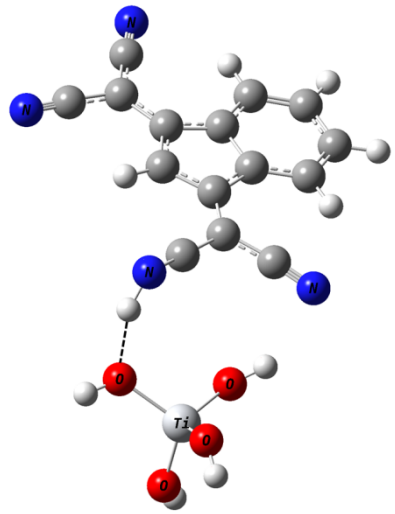
II. Optimized standard coordinates of ground-state for complex 1



C	-2.92351300	3.50376000	-0.28758200
C	-4.13106300	2.91544800	-0.64942100
C	-4.29754700	1.52063400	-0.58812900
C	-3.23118300	0.74229400	-0.15844400
C	-1.99908600	1.34284300	0.20921000
C	-1.83950400	2.71978100	0.14754200
H	-2.80991100	4.58275800	-0.33902900
H	-4.95821900	3.53488500	-0.98308900
H	-5.24432300	1.07652100	-0.87233600
H	-0.90764200	3.19907300	0.42509100
C	-3.07568800	-0.71971700	0.02036100
C	-1.07615700	0.25381500	0.61871000
C	-1.73488700	-0.94332300	0.50235400
C	0.29302800	0.42409000	1.07347400
C	-3.99787800	-1.71733900	-0.21597200
C	0.98678100	1.66691800	1.14420600
N	1.65510700	2.62320200	1.17777700
C	1.09319100	-0.63319200	1.37206900
N	1.81720700	-1.52311200	1.70672300
C	-5.31941300	-1.47075400	-0.69394800
N	-6.39987200	-1.27816900	-1.08449800
C	-3.65365100	-3.08666700	0.01184200
N	-3.35414300	-4.19604600	0.20044400
H	-1.33459900	-1.92225000	0.73358100
Ti	4.57922700	-0.30340900	-0.62955300

O	3.88570700	-1.92213100	-0.00109500
O	6.36920300	-0.41819800	-0.80374200
H	7.05527800	0.03423000	-0.28902700
O	4.11612900	0.92835000	0.56953500
H	3.51203300	1.69479900	0.62983200
O	3.86344400	0.02091800	-2.25134100
H	4.31429700	0.27971400	-3.06958800
H	4.12657100	-2.76338000	-0.42167700
H	2.57725700	-1.91946300	1.09584300

III. Optimized standard coordinates of the first excited state for complex 1



Ti	1.26979700	-0.34772100	-0.03980500
O	1.03313000	0.84258200	-1.45829800
H	1.69428600	1.52786900	-1.64853400
O	-0.28177500	-1.21032900	0.14210600
H	-0.62846500	-2.11499500	0.02590700
O	2.62688300	-1.46022200	-0.44436700
H	3.39981000	-1.69546900	0.09131700
O	1.70282700	0.55916500	1.45517700
H	1.17967900	0.68846200	2.26126500
H	0.02516400	0.36632300	-2.77232900
N	-0.57923700	-0.25567200	-3.36550500
C	-1.58932500	-0.77498100	-2.98428100
C	-2.69521800	-1.46724600	-2.60680800
C	-4.04290200	-1.02412700	-2.91399500
C	-2.38837000	-2.58916000	-1.78542700
C	-5.27970100	-1.61405400	-2.56294700
C	-4.34311700	0.14424100	-3.67054600
N	-2.06315400	-3.45589100	-1.07406600
C	-6.35795600	-0.77700500	-3.12033400
C	-5.59812600	-2.78446600	-1.82716300
C	-5.76516700	0.32267000	-3.80871300
H	-3.60558400	0.81744700	-4.09324900
C	-7.70329900	-1.15161600	-2.91162800
C	-6.92146100	-3.11190600	-1.64878900
H	-4.81506600	-3.40916200	-1.41275000

C	-6.36205500	1.40557500	-4.50617300
C	-7.96883000	-2.29672200	-2.18970500
H	-8.51133100	-0.55114800	-3.31237100
H	-7.18673500	-4.00370400	-1.08902000
C	-7.76377400	1.54996300	-4.62587600
C	-5.54475200	2.39333100	-5.10844700
H	-8.99971100	-2.59567500	-2.02305700
N	-8.92605200	1.64672000	-4.70999800
N	-4.83095100	3.18545700	-5.58746600

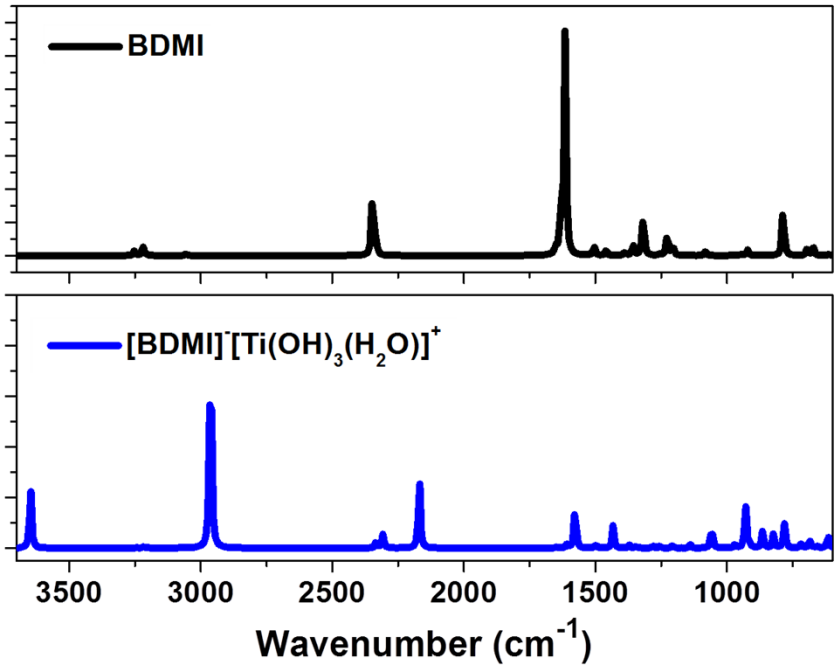
IV. TD-DFT calculation[a] results for complex 1

State	Transition energy	Transition configuration	Oscillator strength (*f*)
S_1	520.9 nm (2.38 eV)	HOMO → LUMO (82%) HOMO-1 → LUMO (17%)	0.0952
S_2	369.4 nm (3.36 eV)	HOMO → LUMO+1 (96%) HOMO-1 → LUMO (2%)	0.0148
S_3	363.7 nm (3.41 eV)	HOMO-1 → LUMO (72%) HOMO → LUMO (15%) HOMO → LUMO+1 (3%) HOMO → LUMO+3 (6%)	0.3694
S_4	356.0 (3.48 eV)	HOMO → LUMO+2 (18%) HOMO → LUMO+3 (69%) HOMO-2 → LUMO+3 (3%) HOMO-1 → LUMO (4%)	0.0208
S_5	348.9 (3.55 eV)	HOMO → LUMO+2 (78%) HOMO → LUMO+3 (14%) HOMO-2 → LUMO (5%)	0.0171
S_6	347.8 (3.56 eV)	HOMO-2 → LUMO (88%) HOMO → LUMO (2%) HOMO → LUMO+2 (2%)	0.2252

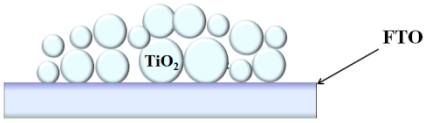
		HOMO → LUMO+3 (3%)	
S_7	288.7 (4.29 eV)	HOMO-1 → LUMO+1 (3%)	0.0003
S_8	287.5 (4.31 eV)	HOMO → LUMO+4 (91%) HOMO-3 → LUMO (4%)	0.0220
S_9	280.0 (4.43 eV)	HOMO → LUMO+5 (95%)	0.0024
S_{10}	277.0 (4.48 eV)	HOMO-1 → LUMO+2 (98%)	0.0000

[a]TD-DFT were calculated at the B3LYP level using LANL2DZ basis set for Ti and 6-31G(d) basis set for all other atoms.

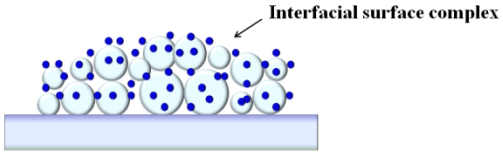
V. Calculated FT-IR results for BDMI and complex 1



VI. Fabrication procedure of DSSCs

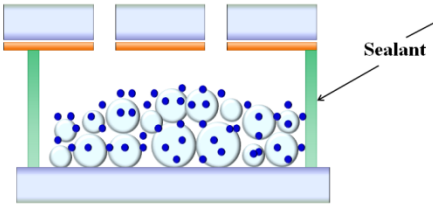


1. TiO_2 paste deposit on FTO glass
   FTO thickness : 200 nm
   Sheet Resistance : 8 Ω/sq
   transmittance : 65%
   Soft dry : 100°C 10 min
   Sintering : 550 °C 60 min

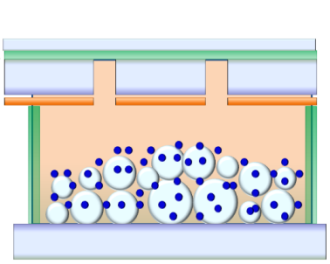


2. BDMI absorption
   3.0 mM BDMI solution
   in EtOH for 20 min

3. Counter electode
   $PtCl_4$: H_2PtCl_6
   + Isopropyl alcohol
   Dry (400°C, 20 min)



4. Sealing
   Sealant (SX 1170 hot melt)
   - 60 um thick spacer



5. Fill with electrolyte and
   measurement
   300 W Xe lamp
   AM-1.5 (100 mW/cm²)