

## Supplementary Information

### High Performance Organic Photosensitizers for Dye-Sensitized Solar Cells

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## Materials.

*N,N'*-Diphenylamino benzaldehyde, cyanoacetic acid, di-*tert*-butyl-*p*-cresol, piperidine, diphenylamine, potassium *tert*-butoxide (1.0M solution in THF), methyltriphenylphosphonium iodide, copper(I) oxide, silver nitrate, and iodine were purchased from Aldrich and used as received. Solvent  
5 such as absolute methanol, *N,N'*-dimethylacetamide (DMAc), and acetonitrile were obtained from Aldrich and used as received. Tetrahydrofuran (THF) was used after distillation under sodium and benzophenone. Spectroscopic-grade solvents from Aldrich were used for spectral measurements. Water was obtained from a Millipore Nanopure water system.

## 10 Instrument

<sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a Varian UNITY INOVA 400 at 400 and 100 MHz, respectively. FT-IR spectra were obtained using Perkin-Elmer System 2000 FR-IR spectrophotometer. MALDI-TOF spectra were obtained using Voyager Biospectrometry time of flight mass spectrometer (Perspective Biosystem) operated at 25 kV accelerating voltage in reflector mode with positive  
15 ionization. Dithranol was used as the matrix. UV-Vis spectra were recorded on Hewlett-Packard 8452A spectrophotometer. HPLC chromatograms were obtained using Hewlett Packard HP1100 with Zorbax Eclipse Plus C18 Column(Agilent Technologies). Differential pulse voltammetry spectra were obtained using a three-electrode cell with CH Instrument (CHI 430A). The measurement was carried out using a Ag/AgCl electrode, a platinum disk and a platinum wire as a reference, a working and a  
20 counter electrode, respectively, in DMF solution containing 0.1 M tetrabutylammonium tetrafluoroborate as a supporting electrolyte. A standard ferrocene/ferrocenium (Fc/Fc<sup>+</sup>) system was used to calibrate the oxidation peak. Photocurrent–voltage were measured using a class-A solar simulator (Yamashita Denso, model YSS-200A) equipped with a 1600W Xenon lamp and AM 1.5G filter, where light intensity was adjusted with a Fraunhofer ISE-calibrated mono Si solar cell with KG-

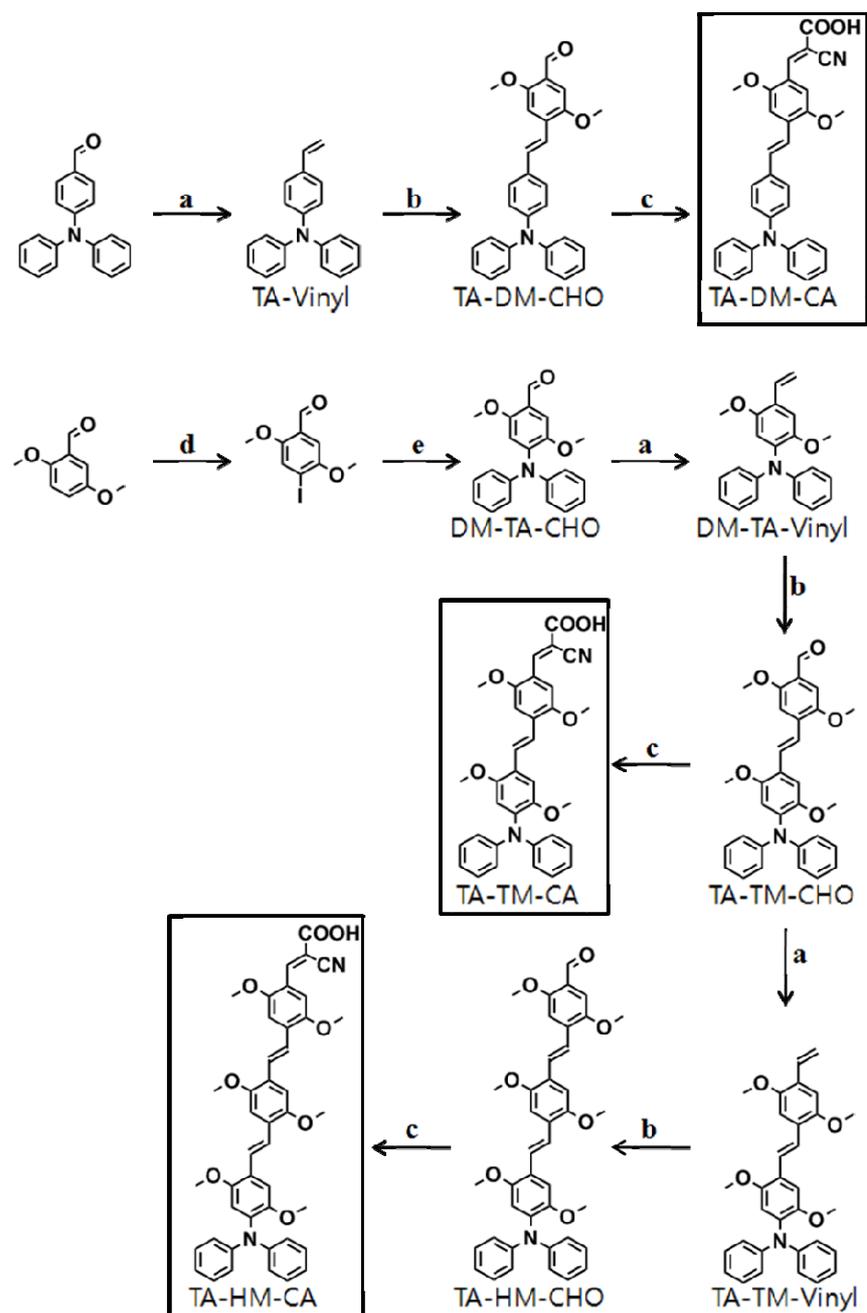
3 filter for approximating 1 sun light intensity. During photocurrent–voltage measurement, DSSC was covered with a black mask with an aperture to avoid additional light coming through lateral space. IPCE was measured as a function of wavelength from 300 to 800 nm using a specially designed IPCE system for dye-sensitized solar cell (PV Measurements, Inc.). A 75W Xenon lamp was used as a light source for generating monochromatic beam. Calibration was performed using a silicon photodiode, which was calibrated using the NIST-calibrated photodiode G425 as a standard, and IPCE values were collected under bias light at a low chopping speed of 10 Hz.

### DSSC fabrication

10 DSSCs were fabricated as follows. FTO-coated conducting glass substrates (TEC8, Pilkington, 8 ohm/square, glass thickness of 2.3 mm) were pre-cleaned ultrasonically in ethanol. The surface on FTO was pre-treated with 0.15M titanium(IV) bis(ethylacetoacetato) diisopropoxide in 1-butanol solution by spin coating, which was sintered at 500 °C for 10 min. The screen printable TiO<sub>2</sub> paste was prepared by mixing the home-made nanocrystalline anatase TiO<sub>2</sub> particles (~ 20 nm) with ethyl cellulose (Aldrich), lauric acid (Fluka) and terpineol (Fluka). The prepared TiO<sub>2</sub> paste was coated on a FTO glass substrate, which was annealed at 500 °C for 30 min. A light scattering overlayer, composed of anatase TiO<sub>2</sub> particles (~400 nm, CCIC), was formed on the nanocrystalline TiO<sub>2</sub> film. The annealed TiO<sub>2</sub> film was treated with 0.2 M TiCl<sub>4</sub> at 30 °C for 16 h, which was heated at 500 °C for 30 min. The annealed nanocrystalline TiO<sub>2</sub> underlayer was determined to be about 10 μm and the scattering overlayer was about 5 μm as measured with Alpha-step IQ surface profiler (KLA Tencor). For dye adsorption, the annealed TiO<sub>2</sub> films were immersed in ethanol containing 0.5 mM of TA-DM-CA, TA-TM-CA and TA-HM-CA for 24 h at ambient temperature. N-719 dye (Ru[LL'(NCS)<sub>2</sub>], L=2,2'-bipyridyl-4,4'-dicarboxylic acid, L'=2,2'-bipyridyl-4,4'-ditetabutylammonium carboxylate) was also used for comparison. A counter electrode was prepared by dropping a 7 mM of H<sub>2</sub>PtCl<sub>6</sub>

solution on a FTO substrate, which was heated at 400 °C for 20 min to form the metallic Pt nanoparticles. The dye-adsorbed TiO<sub>2</sub> working electrode and the Pt counter electrode were sealed with a 25- $\mu$ m-thick surlyn (Dupont 1702). An electrolyte solution was introduced through a drilled hole on the counter electrode, where the electrolyte solution was composed of 0.7 M 1-propyl-3-methylimidazolium iodide (PMII), 0.05 M I<sub>2</sub>, 0.2 M LiI and 0.5 M 4-*tert*-butylpyridine in the mixture of acetonitrile and valeronitrile (v/v, 85:15). The active area of dye coated TiO<sub>2</sub> film was about 0.27 cm<sup>2</sup> as measured by an image analysis program equipped with a digital microscope camera (Moticam 1000). A black mask with an aperture being close to the active area was put on the DSSC while measuring under 1 sun illumination.

## Synthesis of Organic Dyes



**Fig. 1** (a) THF, KO(t-Bu),  $\text{CH}_3\text{PPh}_3\text{I}$ , rt, 4h; (b) DMAc, 4-iodo-2,5-dimethoxybenzaldehyde,  $\text{Na}_2\text{CO}_3$ , Pd cat.,  $130^\circ\text{C}$ , 24h; (c) Acetonitrile, cyanoacetic acid, piperidine,  $90^\circ\text{C}$ , 24h; (d) Methanol,  $\text{AgNO}_3$ ,  $\text{I}_2$ , rt, 7h; (e) DMAc, diphenylamine,  $\text{Cu}_2\text{O}$ ,  $190^\circ\text{C}$ , 3days.

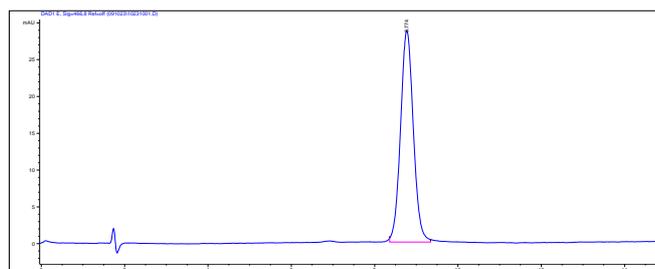
### Synthesis of TA-DM-CHO.

4-Iodo-2,5-dimethoxybenzaldehyde and TA-Vinyl were prepared by following a reference procedure.<sup>1,2</sup> A DMAc solution of TA-Vinyl (0.86 g, 3.15 mmol), 4-iodo-2,5-dimethoxybenzaldehyde (1.10 g, 3.78 mmol), sodium carbonate (0.84 g, 7.88 mmol), 2,6-di-*tert*-butylcresol (0.14 g, 0.63 mmol), and trans-di( $\mu$ -acetato)bis[o-(di-*o*-tolylphosphino)benzyl] dipalladium(II) (29.56mg, 0.03mmol) was stirred at 130°C for 24 h under nitrogen. After cooling, the solution was poured into a mixture of methylene chloride and distilled water. The product mixture extracted in the organic layer was purified by column chromatography on a silica gel using n-hexane/methylene chloride (4:1, v/v) as an eluent. Further purification was performed by repeated precipitation from methylene chloride into methanol to give TA-DM-CHO as an orange solid. (Yield 1.10g, 69 %). <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  3.83 (s, 3H, -Ph-O-CH<sub>3</sub>), 3.95 (s, 3H, -Ph-O-CH<sub>3</sub>), 6.95 (d, *J*=8.4Hz, 2H, -Ph-N-Ph<sub>2</sub>), 7.04 (d, *J*=8.4Hz, 4H, -N-Ph<sub>2</sub>), 7.08 (t, *J*=7.7Hz, 2H, -N-Ph<sub>2</sub>), 7.29 (d, *J*=16.5Hz, 1H, -CH=CH-Ph-), 7.32 (dd, *J*=7.7, 8.4Hz, 4H, -N-Ph<sub>2</sub>), 7.38 (s, 1H, =CH-Ph-CH=), 7.40 (d, *J*=16.5Hz, 1H, -CH=CH-Ph-), 7.50 (d, *J*=8.4Hz, 2H, -Ph-N-Ph<sub>2</sub>), 7.54 (s, 1H, =CH-Ph-CH=), 10.29 (s, 1H, CHO-Ph-); <sup>13</sup>CNMR (100.64 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  55.87, 56.35, 108.54, 109.77, 119.67, 122.25, 122.80, 123.43, 124.35, 127.90, 129.49, 130.60, 132.27, 133.87, 146.61, 147.26, 150.29, 156.10, 187.70.

### Synthesis of TA-DM-CA.

An acetonitrile solution of TA-DM-CHO (1.50 g, 2.98 mmol), cyanoacetic acid (5.08 g, 59.69 mmol) and piperidine (5.08g, 59.69 mmol) was stirred at 90°C for 24 h under nitrogen. After cooling, the solution was poured into a mixture of methylene chloride and aqueous solution of pH 2 (adjusted by phosphoric acid). The organic layer was separated and dried over Na<sub>2</sub>SO<sub>4</sub>. After removal of the solvent at reduced pressure, the crude product was purified by column chromatography over silica gel

using THF/methylene chloride (3:1, v/v) as an eluent. Further purification was performed by precipitation from methylene chloride into n-hexane (1:20, v/v) to obtain TA-DM-CA as a red solid. A single peak was shown from the HPLC chromatogram. (Yield 0.76g, 44 %), mp 260-262°C.  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO-}d_6$ )  $\delta$  3.83 (s, 3H, -Ph-O-CH<sub>3</sub>), 3.88 (s, 3H, Ph-O-CH<sub>3</sub>), 6.95 (d,  $J=8.4\text{Hz}$ , 2H, -Ph-N-Ph<sub>2</sub>), 7.04 (d,  $J=8.4\text{Hz}$ , 4H, -N-Ph<sub>2</sub>), 7.06 (t,  $J=7.7\text{Hz}$ , 2H, -N-Ph<sub>2</sub>), 7.29 (d,  $J=16.5\text{Hz}$ , 1H, -CH=CH-Ph-), 7.32 (dd,  $J=7.7, 8.4\text{Hz}$ , 4H, -N-Ph<sub>2</sub>), 7.38 (s, 1H, =CH-Ph-CH=), 7.40 (d,  $J=16.5\text{Hz}$ , 1H, -CH=CH-Ph-), 7.50 (d,  $J=8.4\text{Hz}$ , 2H, -Ph-N-Ph<sub>2</sub>), 7.54 (s, 1H, =CH-Ph-CH=), 7.65 (s, 1H, -C=CH-Ph-);  $^{13}\text{C}$  NMR (100.64 MHz,  $\text{DMSO-}d_6$ )  $\delta$  55.90, 56.46, 110.18, 122.34, 123.59, 124.48, 124.51, 128.07, 128.12, 129.65, 130.74, 146.76, 147.43, 150.07, 153.57, 163.63; MALDI-TOF (MW = 502.56)  $m/z$  503.73 [m+H]<sup>+</sup>.



### Synthesis of DM-TA-CHO.

A DMAc solution (60mL) of 4-iodo-2,5-dimethoxy benzaldehyde (4.00 g, 13.70 mmol), diphenyl amine (2.78 g, 16.44 mmol), and copper(I) oxide (2.35 g, 16.44 mmol) was stirred at 190°C for 3 days. After cooling to room temperature, the product mixture was washed with methylene chloride and water. The organic layer was concentrated by vacuum evaporator. The residue was purified by column chromatography on silica gel using methylene chloride and n-hexane (1:5, v/v) as an eluent. Further purification was performed by precipitation from methylene chloride into n-hexane to obtain DM-TA-CHO as a light yellow solid. Yield (1.053 g, 23%). mp, 148~150°C.  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO-}d_6$ )  $\delta$

3.51 (s, 3H, -OCH<sub>3</sub>), 3.68 (s, 3H, -OCH<sub>3</sub>), 6.78 (s, 1H, CHO-Ph-N), 6.92 (d, *J* = 8.4 Hz, 4H, -N-Ph<sub>2</sub>), 7.02 (t, *J* = 7.3 Hz, 2H, -N-Ph<sub>2</sub>), 7.27 (dd, *J* = 7.3, 8.4 Hz, 4H, -N-Ph<sub>2</sub>), 10.24 (s, 1H, -CHO); <sup>13</sup>C NMR (100.64 MHz, DMSO-*d*<sub>6</sub>) δ 56.10, 56.29, 110.79, 111.87, 120.90, 123.05, 123.16, 128.93, 143.66, 147.09, 148.54, 157.44, 188.09.

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### Synthesis of DM-TA-Vinyl.

A THF solution (40 ml) of DM-TA-CHO (1.00 g, 3.00 mmol) was added to a THF solution of potassium *tert*-butoxide (3.60 ml, 3.60 mmol) and methyl triphenyl phosphonium iodide (1.46 g, 3.60 mmol). The solution was then stirred at room temperature for 4 h under nitrogen. The solution was poured into a mixture of methylene chloride and distilled water. The product mixture extracted in the organic layer was purified by column chromatography on silica gel using n-hexane as an eluent. After removal of the solvent, the residue was precipitated from methylene chloride into methanol to give DM-TA-Vinyl as a white solid. Yield (782 mg, 79%). mp, 113~115°C. <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) δ 3.58 (s, 3H, Ph-O-CH<sub>3</sub>), 3.68 (s, 3H, Ph-O-CH<sub>3</sub>), 5.26 (d, *J*=11.0 Hz, 1H, -CH=CH<sub>2</sub>), 5.71 (d, *J*=17.6 Hz, 1H, -CH=CH<sub>2</sub>), 6.68 (s, 1H, =CH-Ph-N-), 6.94 (t, *J*=7.7 Hz, 2H, -N-Ph<sub>2</sub>), 7.02 (d, *J*=7.7 Hz, 4H, -N-Ph<sub>2</sub>), 7.02 (dd, *J*=11.0, 17.6 Hz, 1H, -CH=CH<sub>2</sub>), 7.09 (s, 1H, =CH-Ph-N), 7.20 (t, *J*=7.7 Hz, 4H, -N-Ph<sub>2</sub>); <sup>13</sup>C NMR (100.64 MHz, DMSO-*d*<sub>6</sub>) δ 56.28, 56.92, 112.39, 112.78, 113.92, 121.62, 121.68, 124.44, 128.75, 131.04, 136.04, 147.34, 149.89, 151.75.

### Synthesis of TA-TM-CHO.

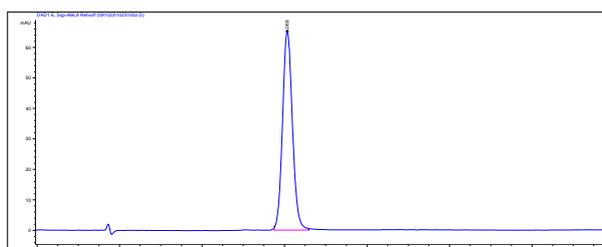
A THF solution (40mL) of DM-TA-Vinyl (750mg, 2.26 mmol), 4-iodo-2,5-dimethoxy benzaldehyde (727 mg, 2.49 mmol), sodium carbonate (720 mg, 6.79 mmol), 2,6-di-*tert*-butyl-*p*-cresol (99.70 mg, 0.45 mmol), and trans-di(μ-acetato)bis[o-(di-*o*-tolylphosphino)benzyl]

dipalladium(II) (21.20 mg, 0.23  $\mu\text{mol}$ ) was stirred at 110°C for 24 h. After evaporation the solvent, the mixture was poured into methylene chloride and water. After concentration of the organic layer, the residue was purified by column chromatography on silica gel using methylene chloride and n-hexane (1:5, v/v) as an eluent. Yield (664 mg, 60%). mp, 214~216°C.  $^1\text{H}$  NMR (400 MHz, DMSO- $d_6$ )  $\delta$  3.60 (s, 3H, -Ph-O- $\text{CH}_3$ ), 3.69 (s, 3H, -Ph-O- $\text{CH}_3$ ), 3.85 (s, 3H, -Ph-O- $\text{CH}_3$ ), 3.96 (s, 3H, -Ph-O- $\text{CH}_3$ ), 6.77 (s, 1H, =CH-*Ph*-N-), 6.94 (t,  $J=7.7$  Hz, 2H, -N- $\text{Ph}_2$ ), 7.02 (d,  $J=7.7$  Hz, 4H, -N- $\text{Ph}_2$ ), 7.20 (t,  $J=7.7$  Hz, 4H, -N- $\text{Ph}_2$ ), 7.21 (s, 1H, =CH-*Ph*-N-), 7.34 (s, 1H, CHO-*Ph*-CH=), 7.40 (s, 1H, CHO-*Ph*-CH=), 7.46 (d,  $J=16.5$  Hz, 1H, -Ph-CH=CH-*Ph*-), 7.62 (d,  $J=16.5$  Hz, 1H, -Ph-CH=CH-*Ph*-), 10.31 (s, 1H, CHO-*Ph*-);  $^{13}\text{C}$  NMR (100.64 MHz, DMSO- $d_6$ )  $\delta$  55.93, 56.13, 56.24, 56.40, 93.88, 108.60, 110.57, 112.90, 121.08, 121.60, 122.95, 123.11, 123.80, 127.59, 128.90, 134.19, 135.36, 146.67, 149.67, 150.57, 151.84, 156.07, 187.78.

### Synthesis of TA-TM-CA.

An acetonitrile solution (50 ml) of TA-TM-CHO (600 mg, 1.21 mmol), cyanoacetic acid (2.06 g, 24.22 mmol), and piperidine (2.06 g, 24.22 mmol) was stirred at 90°C for 24 h. The mixture solution was cooled at room temperature then washed with methylene chloride and phosphoric acid aqueous (2.0 M in water). The organic phase was concentrated under reduced pressure. The residue was purified by column chromatography on silica gel using methylene chloride and THF (1:5, v/v) as an eluent. A single peak was shown from the HPCL chromatogram. Yield (411 mg, 60%). mp, 260~264°C.  $^1\text{H}$  NMR (400 MHz, DMSO- $d_6$ )  $\delta$  3.60 (s, 3H, -Ph-O- $\text{CH}_3$ ), 3.69 (s, 3H, -Ph-O- $\text{CH}_3$ ), 3.83 (s, 3H, -Ph-O- $\text{CH}_3$ ), 3.90 (s, 3H, -Ph-O- $\text{CH}_3$ ), 6.77 (s, 1H, =CH-*Ph*-N-), 6.89 (t,  $J=7.7$  Hz, 2H, -N- $\text{Ph}_2$ ), 6.93 (d,  $J=7.7$  Hz, 4H, -N- $\text{Ph}_2$ ), 7.23 (t,  $J=7.7$  Hz, 4H, -N- $\text{Ph}_2$ ), 7.29 (s, 1H, =CH-*Ph*-N-),

7.34 (s, 1H, =CH-*Ph*-CH=), 7.45 (d,  $J=16.5$  Hz, 1H, -CH=CH-*Ph*-N-), 7.56 (d,  $J=16.5$  Hz, 1H, -  
CH=CH-*Ph*-N-), 7.81 (s, 1H, =CH-*Ph*-CH=), 8.32 (s, 1H, =CH-*Ph*-CH=);  $^{13}\text{C}$  NMR (100.64 MHz,  
DMSO- $d_6$ )  $\delta$  55.91, 56.13, 56.24, 56.40, 102.87, 109.36, 110.33, 112.35, 112.97, 119.44, 120.91,  
121.04, 121.56, 123.38, 124.14, 124.77, 125.83, 128.91, 130.23, 135.00, 146.70, 149.74, 150.17,  
5 151.69, 152.28, 163.92; MALDI-TOF (MW = 562.61)  $m/z$  562.50 [m+H] $^+$ .



### Synthesis of TA-TM-Vinyl.

A THF solution of potassium *tert*-butoxide-1.0M (1.60 ml, 1.600 mmol ) was added into a THF  
10 solution (40 ml) of TA-TM-CHO (650 mg, 1.31 mmol) and methyl triphenylphosphonium iodide  
(636 mg, 1.57 mmol). The reaction mixture was stirred at room temperature for 4 h. After removal of  
the solvent, the mixture was washed with methylene chloride and water. After removal of the solvent  
from the organic layer, the residue was purified by column chromatography on a silica gel using  
methylene chloride and n-hexane (1:5, v/v) as an eluent. Yield (305 mg, 47%). mp, 128~130°C.  $^1\text{H}$   
15 NMR (400 MHz, DMSO- $d_6$ )  $\delta$  3.60 (s, 3H, -Ph-O- $\text{CH}_3$ ), 3.68 (s, 3H, -Ph-O- $\text{CH}_3$ ), 3.83 (s, 3H, -Ph-  
O- $\text{CH}_3$ ), 3.84 (s, 3H, -Ph-O- $\text{CH}_3$ ), 5.26 (d,  $J=11.0$  Hz, 1H, -CH=CH $_2$ ), 5.71 (d,  $J=16.5$  Hz, 1H, -  
CH=CH $_2$ ), 6.76 (s, 1H, =CH-*Ph*-N-), 6.88 (d,  $J=16.5$  Hz, 1H, -Ph-CH=CH-*Ph*-), 6.91 (t,  $J=7.7$  Hz,  
2H, -N-*Ph* $_2$ ), 6.93 (d,  $J=7.7$  Hz, 4H, -N-*Ph* $_2$ ), 7.02 (dd,  $J=11.0, 17.7$  Hz, 1H, -CH=CH $_2$ ), 7.18 (d,  
 $J=16.5$  Hz, 1H, -Ph-CH=CH-*Ph*-), 7.22 (t,  $J=7.7$  Hz, 4H, -N-*Ph* $_2$ ), 7.23 (s, 1H, =CH-*Ph*-N-), 7.31 (s,  
20 1H, CH $_2$ =CH-*Ph*-CH=), 7.41 (s, 1H, CH $_2$ =CH-*Ph*-CH=);  $^{13}\text{C}$  NMR (100.64 MHz, DMSO- $d_6$ )  $\delta$   
56.25, 56.39, 56.47, 57.02, 109.23, 110.04, 112.27, 112.67, 113.36, 113.86, 114.08, 116.76, 121.51,

121.66, 122.99, 124.68, 126.58, 127.33, 128.73, 131.35, 135.89, 147.36, 149.98, 151.19.

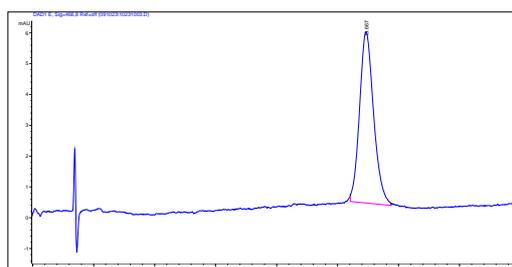
### Synthesis of TA-HM-CHO.

A DMAc solution (40 ml) of TA-TM-Vinyl (300 mg, 0.61 mmol), 4-iodo-2,5-dimethoxy benzaldehyde (213 mg, 0.73 mmol), sodium carbonate (193 mg, 1.82 mmol), 2,6-di-*tert*-butyl-*p*-cresol (26.80 mg, 0.12 mmol), and trans-di( $\mu$ -acetato)bis[o-(di-*o*-tolylphosphino)benzyl] dipalladium(II) (6 mg, 6.08  $\mu$ mol) was stirred at 130°C for 24 h. After removal of the solvent, the mixture was washed with methylene chloride and water. After removal of the organic solvent, the residue was purified by column chromatography on a silica gel using methylene chloride and *n*-hexane (1:5, v/v) as an eluent. Yield (230 mg, 58%). mp, 198~200°C. <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  3.62 (s, 3H, -Ph-O-CH<sub>3</sub>), 3.67 (s, 3H, -Ph-O-CH<sub>3</sub>), 3.83 (s, 3H, -Ph-O-CH<sub>3</sub>), 3.87 (s, 3H, -Ph-O-CH<sub>3</sub>), 3.91 (s, 3H, -Ph-O-CH<sub>3</sub>), 3.93 (s, 3H, -Ph-O-CH<sub>3</sub>), 6.77 (s, 1H, =CH-*Ph*-N-), 6.91 (s, 1H, =CH-*Ph*-N-), 6.92 (d, *J*=7.7 Hz, 4H, -N-*Ph*<sub>2</sub>), 6.93 (t, *J*=7.7 Hz, 2H, -N-*Ph*<sub>2</sub>), 7.23 (t, *J*=7.7 Hz, 4H, -N-*Ph*<sub>2</sub>), 7.31 (s, 1H, =CH-*Ph*-CH=), 7.32 (s, 1H, =CH-*Ph*-CH=), 7.39 (d, *J*=16.8 Hz, 1H, -Ph-CH=CH-*Ph*-), 7.44 (s, 1H, =CH-*Ph*-O-CH<sub>3</sub>), 7.45 (s, 1H, =CH-*Ph*-O-CH<sub>3</sub>), 7.47 (d, *J*=16.8 Hz, 1H, -Ph-CH=CH-*Ph*-), 7.50 (d, *J*=16.5 Hz, 1H, -Ph-CH=CH-*Ph*-), 7.59 (d, *J*=16.5 Hz, 1H, -Ph-CH=CH-*Ph*-), 9.95 (s, 1H, CHO-*Ph*-CH=); <sup>13</sup>C NMR (100.64 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  56.18, 56.38, 100.66, 101.11, 109.50, 109.77, 116.00, 116.58, 120.94, 121.47, 123.67, 123.94, 124.61, 125.64, 126.75, 128.82, 129.07, 130.73, 134.46, 140.12, 140.58, 141.29, 146.92, 149.82, 150.95, 151.21, 151.46, 161.36, 161.46, 187.95.

### Synthesis of TA-HM-CA.

Piperidine (1.42 g, 0.17 mmol) was added into an acetonitrile solution (30 ml) of TA-HM-CHO

(200 mg, 0.30 mmol) and cyanoacetic acid (580 mg, 6.82 mmol). The solution was stirred at 90°C for 24 h. After removal of the solvent, the reaction mixture was washed with methylene chloride and phosphoric acid aqueous (2.0 M in water). After removal of the solvent from the organic layer, the product mixture was purified by column chromatography on silica gel using methylene chloride and THF (1:5, v/v) as an eluent. A single peak was shown from the HPCL chromatogram. Yield (157 mg, 71%). mp, 279~281°C. <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) δ 3.61 (s, 3H, -Ph-O-CH<sub>3</sub>), 3.69 (s, 3H, -Ph-O-CH<sub>3</sub>), 3.85 (s, 3H, -Ph-O-CH<sub>3</sub>), 3.89 (s, 3H, -Ph-O-CH<sub>3</sub>), 3.90 (s, 3H, -Ph-O-CH<sub>3</sub>), 3.91 (s, 3H, -Ph-O-CH<sub>3</sub>), 6.77 (s, 1H, =CH-*Ph*-N-), 6.91 (s, 1H, =CH-*Ph*-N-), 6.92 (d, *J*=7.7 Hz, 4H, -N-*Ph*<sub>2</sub>), 6.93 (t, *J*=7.7 Hz, 2H, -N-*Ph*<sub>2</sub>), 7.23 (t, *J*=7.7 Hz, 4H, -N-*Ph*<sub>2</sub>), 7.31 (s, 1H, =CH-*Ph*-CH=), 7.32 (s, 1H, =CH-*Ph*-CH=), 7.39 (d, *J*=16.8 Hz, 1H, -Ph-CH=CH-*Ph*-), 7.44 (s, 1H, =CH-*Ph*-O-CH<sub>3</sub>), 7.45 (s, 1H, =CH-*Ph*-O-CH<sub>3</sub>), 7.47 (d, *J*=16.8 Hz, 1H, -Ph-CH=CH-*Ph*-), 7.50 (d, *J*=16.5 Hz, 1H, -Ph-CH=CH-*Ph*-), 7.59 (d, *J*=16.5 Hz, 1H, -Ph-CH=CH-*Ph*-), 8.28 (s, 1H, =CH-*Ph*-CH=); <sup>13</sup>C NMR (100.64 MHz, DMSO-*d*<sub>6</sub>) δ 56.18, 56.38, 100.66, 101.11, 109.50, 109.77, 110.13, 116.00, 116.56, 120.94, 121.47, 123.67, 123.94, 124.61, 125.64, 126.75, 128.82, 128.88, 129.08, 130.75, 134.48, 140.12, 140.57, 141.30, 146.71, 146.94, 149.80, 150.90, 151.21, 151.46, 161.36, 161.46; MALDI-TOF MS (MW = 724.80) *m/z* 724.85 [m+H]<sup>+</sup>.



## Reference

- 1 B. A. Hathaway, K. L. White, M. E. McGill, *synthetic communication*, 2007, **37**, 3855

2 S. Hwang, J. H. Lee, C. Park, H. Lee, C. Kim, C. Park, M. H. Lee, W. Lee, J. Park, K. Kim, N. G.

Park and C. Kim, *Chem. Commun.*, 2007, 4887