Electronic Supporting Information

Substituent Effect of Ru(II) Based Sensitizers Bearing Terpyridine Anchor and Pyridyl Azolate Ancillary for Dye Sensitized Solar Cells

Ting-Kuang Chang,^{a,‡} Huiyang Li,^{b,‡} Kuan-Ting Chen,^a Yi-Chou Tsai,^{a,*} Yun Chi,^{a,*} Ting-Yun Hsiao,^c and Ji-Jung Kai,^{c,*}

^a Department of Chemistry and Low Carbon Energy Research Center, National Tsing Hua University, Hsinchu 30013, Taiwan; E-mail: <u>yictsai@mx.nthu.edu.tw</u> and <u>ychi@mx.nthu.edu.tw</u>

^b Department of Chemistry, Hubei Key Lab on Organic and Polymeric Opto-Electronic Materials, Wuhan University, Wuhan 430072, China

^c Department of Engineering and System Science, National Tsing Hua University, Hsinchu 30013, Taiwan; E-mail: jjkai@ess.nthu.edu.tw

[†] These authors have equal contribution.

Procedures for Device measurement

Photovoltaic measurements were tested under a class-AAA solar simulator (Model 11016A, Sun 3000, ABET Technologies) equipped with a 550 W xenon light source and water-cooling stage (25 °C). The output power density was calibrated to be 100 mW/cm² using a certificated KG-5 Si reference cell and with a circular aperture of 8 mm. The current-voltage characteristic of each cell was obtained with adopting 4-wire sense mode, delay time set as 100 ms and bias scan from shortcircuit to open-circuit by using a Keithley digital source meter (Model 2400). The spectra of incident photon-to-current conversion efficiency (IPCE) were calculated with the equation of $1240 \cdot J_{SC}(\lambda)/(\lambda \cdot P_{in}(\lambda))$ where J_{SC} is the short-circuit current density under each monochromatic illumination in unit of A/cm², λ is the wavelength of incident monochromatic light in unit of nanometer, and Pin is the monochromatic light intensity in unit of W/cm² and were plotted as a function of incident wavelength with an increment of 10 nm. The current was pre-amplified by a current amplifier (SR570) and measured by Keithley 2400. It should be noted that 10 values of J_{SC} (interval 50 ms) were collected sequentially after illuminating the device for 3 seconds and then averaged for calculation of IPCE. A 300 W Xe lamp (Model 6258, Newport Oriel) combined with an Oriel cornerstone 260 1/4 m monochromator (Model 74100) provided a device under test with a monochromatic beam (DC mode). The beam power intensity was calibrated with a power meter (Model 1936-C, Newport) equipped with a Newport 818-UV photodetector.

Photophysical measurements of DSC devices.

Charge extraction (CE) was measured with the PGSTAT302N electrochemical workstation (Autolab) at an open-circuit condition for the photovoltage of the device to attain a steady state. The red light-emitting diode (LED, 627 nm) was switched off while the device was simultaneously switched to a short-circuit condition to measure the excess charges generated in the film. Intensity-modulated photovoltage spectroscopy (IMVS) measurement was conducted using the same electrochemical workstation equipped with a frequency response analyzer (FRA) to drive a red light emitting diode. The analysis of the photovoltage response of the cells was conducted in the frequency range of $10^4 - 1$ Hz and LED supplied the AC (modulation depth 10%) perturbation current superimposed on the DC current.

Cyclic voltammetry.

The oxidation and reduction measurements were recorded using glassy carbon as the working electrode at the scan rate of 50 mV s⁻¹. All electrochemical potentials were measured in a 0.1 M TBAPF₆ solution in DMF for both oxidation and reduction reaction, and reported in volts against an Ag/Ag⁺ (0.01 M AgNO₃) reference electrode with ferrocene (FcH) as the internal standard; ΔE_p is defined as E_{pa} (anodic peak potential) – E_{pc} (cathodic peak potential) and these data are quoted in mV.

General Statement for Ligand Preparation.

Mass spectra were obtained on a JEOL SX-102A instrument operating in electron impact (EI) mode or fast atom bombardment (FAB) mode. ¹H, ¹⁹F NMR spectra were obtained using the Varian Mercury-400 instruments. Elemental analyses were performed using the Heraeus CHN-O rapid elementary analyzer. All reactions were carried out under N₂ atmosphere and anhydrous conditions.

Synthesis of ancillary chelates L2 and L3.



Scheme 1. (i) 2-(tributylstanny)thiophene, Pd(PPh₃)₄, toluene, reflux; (ii) NBS, DMF; (iii) ethyl acetate, NaOEt, reflux; (iv) HCl, reflux; (v) NaOEt, CF₃CO₂Et, N₂H₄·H₂O, reflux; (vi) 3,4-dihydro-2H-pyran, CF₃CO₂H, toluene, reflux; (vii) K₂CO₃, Pd(PPh₃)₄, THF/H₂O, reflux; (viii) CF₃CO₂H, CH₂Cl₂, R.T.; (ix) 4,7-dibromo-2,1,3-benzothidiazole, K₂CO₃, Pd(PPh₃)₄, THF/H₂O, reflux; (x) bis(pinacolato)diboron, Pd(dppf)Cl₂, KOAc, 1,4dioxane.

Synthesis of 2

A mixture of 2-(tributylstanny)thiophene (22 mmol, 8.21 g), ethyl 4-chloropicolinate

(20 mmol, 3.43 g) and $Pd(PPh_3)_4$ (0.05 eq) in toluene (40 mL) was heated under reflux for 10 h. After cooling to RT, the solvent was removed under reduced pressure, and the residue was purified using column chromatography to give **2** as a white solid (3.70 g, 84.4%).

Spectral data of **2**: ¹H NMR (400 MHz, CDCl₃, 298 K): δ 8.70 (d, *J* = 5.2 Hz, 1H), 8.33 (s, 1H), 7.64 (d, *J* = 5.2 Hz, 1H), 7.60 (d, *J* = 4.0 Hz, 1H), 7.47 (d, *J* = 4.8 Hz, 1H), 7.18-7.15 (m, 1H), 4.04 (s, 3H).

Synthesis of 3

To a solution of **2** (970 mg, 4.42 mmol) in DMF (50 mL) was added NBS (945 mg, 5.31 mmol) in three portions at 0 °C. The solution was stirred at RT for 12 h. Then it was poured into water (200 mL) and filtered. The precipitates was washed with water and further purified through recrystallization to give **3** as a white solid (1.11 g, 89%). Spectral data of **3**: ¹H NMR (400 MHz, CDCl₃, 298 K): δ 8.71 (d, *J* = 5.2 Hz, 1H), 8.24 (dd, *J* = 2.0 Hz, *J* = 0.8 Hz, 1H), 7.54 (dd, *J* = 5.2 Hz, *J* = 2.0 Hz, 1H), 7.35 (d, *J* = 3.6 Hz, 1H), 4.04 (s, 3H).

Synthesis of 4

To a solution of **3** (2.98 g, 10.0 mmol) in ethyl acetate (50 mL) was added NaOEt (800 mg, 12.0 mmol). The resultant mixture was stirred under reflux overnight. After cooling to RT, HCl (10 mL) was added and the solution was heated under reflux. After one hour, NaOH (1M) was added to neutralize the acid. The mixture was extracted with ethyl acetate and dried over anhydrous Na₂SO₄. The solution was evaporated to dryness and the residue was purified using column chromatography to give **4** as a white solid (1.90 g, 67%). Spectral data of **4**: ¹H NMR (400 MHz, CDCl₃, 298 K): δ 8.65 (d, *J* = 5.2 Hz, 1H), 8.14 (d, *J* = 1.6 Hz, 1H), 7.53 (dd, *J* = 5.2 Hz, *J* = 2.0 Hz, 1H), 7.35 (d, *J* = 4.0 Hz, 1H), 7.12 (d, *J* = 4.0 Hz, 1H), 2.75 (s, 3H).

Synthesis of 5

To a solution of **4** (170 mg, 0.60 mmol) in THF (10 mL) was added a solution of NaOEt in THF at 0 °C. After stirring for 30 min, ethyl trifluoroacetate (0.1 mL) was added and the solution was heated under reflux for 5 h. After cooling to RT, the solvent was removed under reduced pressure. The residue was added to water, titrated with 2M HCl solution to pH = 3 and extracted with ethyl acetate (20 mL). The solvent was evaporated and the residue was heated with N₂H₄·H₂O (0.3 mL) in ethanol (10 mL) at reflux for 9h. After then, the ethanol was removed and the residue was purified using column chromatography to give **5** as a white solid (80 mg, 36%).

Spectral data of **5**: ¹H NMR (400 MHz, d_6 -acetone, 298 K): δ 13.45 (s, br, 1H), 8.63 (d, J = 5.2 Hz, 1H), 8.22 (s, 1H), 7.72 (d, J = 4.0 Hz, 1H), 7.58 (dd, J = 5.2 Hz, J = 2.0 Hz, 1H), 7.42 (s, 1H), 7.31 (dd, J = 4.0 Hz, J = 0.8 Hz, 1H). ¹⁹F NMR (376 MHz, d_6 -acetone, 298K): δ -62.61 (s, 3F).

Synthesis of 6

To a solution of **5** (180 mg, 0.48 mmol) and CF_3CO_2H (0.5 mL) in toluene (5 mL) was added a solution of 3,4-dihydro-2H-pyran (1 mL) in toluene (5 mL) slowly. The mixture was heated under reflux for 2 h. After cooling to RT, the solvent was removed and residue was purified using column chromatography to give **6** as a white solid (200 mg, 90%).

Spectral data of **6**: ¹H NMR (400 MHz, CDCl₃, 298 K): δ 8.58 (d, *J* = 5.6 Hz, 1H), 8.17 (d, *J* = 1.6 Hz, 1H), 7.36 - 7.35 (m, 2H, ArH), 7.33 (dd, *J* = 5.2 Hz, *J* = 2.0 Hz, 1H), 7.11 (d, *J* = 4.0 Hz, 1H), 5.50 (dd, *J* = 5.6 Hz, *J* = 2.4 Hz, 1H), 4.14 - 4.12 (m, 1H), 3.74-3.69 (m, 1H), 2.68 - 2.60 (m, 1H), 2.17 - 2.15 (m, 1H), 2.04 - 2.00 (m, 1H), 1.82 - 1.62 (m, 3H). ¹⁹F NMR (376 MHz, CDCl₃, 298K): δ -59.42 (s, 3F).

Synthesis of 7

To a mixture of HexylOTPA-B (480 mg, 0.84 mmol), **6** (321 mg, 0.70 mmol), $Pd(PPh_3)_4$

– S6 –

(0.05 eq) in THF (15 mL) was added a solution of K_2CO_3 (2M, 5 mL). After refluxing overnight, the mixture was poured into water, extracted with CH_2Cl_2 , dried over Na_2SO_4 , and evaporated to dryness. The residue was purified using column chromatography to give **7** as a yellow solid (415 mg, 72%).

Spectral data of **7**: ¹H NMR (400 MHz, CDCl₃, 298 K): δ 8.56 (d, *J* = 5.2 Hz, 1H), 8.24 (s, 1H), 7.55 (d, *J* = 4.0 Hz, 1H), 7.45 - 7.41 (m, 3H), 7.37 (s, 1H), 7.21 (d, *J* = 3.6 Hz, 1H), 7.07 (d, *J* = 8.8 Hz, 4H), 6.93 (d, *J* = 8.4 Hz, 2H), 6.84 (d, *J* = 9.2 Hz, 4H), 5.50 (dd, *J* = 5.6 Hz, *J* = 2.4 Hz, 1H), 4.15 - 4.12 (m, 1H), 3.94 (t, *J* = 6.4 Hz, 4H), 3.75 - 3.69 (m, 1H), 2.70 - 2.61 (m, 1H), 2.19 - 2.15 (m, 1H), 2.05 - 2.02 (m, 1H), 1.82 - 1.62 (m, 7H), 1.51 - 1.43 (m, 4H), 1.37 - 1.33 (m, 8H), 0.91 (t, *J* = 6.8 Hz, 6H).

Synthesis of L2H

A solution of **7** (415 mg, 0.52 mmol) and CF_3CO_2H (5 mL) in CH_2Cl_2 (15 mL) was stirred at RT for 9 h. Then, it was poured into water and neutralized with a saturated NaHCO₃ solution. The mixture was extracted with CH_2Cl_2 , washed with water and dried with Na₂SO₄. After removal of solvent, and the residue was purified using column chromatography to give **L2H** as a yellow solid (330 mg, 88%).

Spectral data of L2H: ¹H NMR (400 MHz, d_6 -acetone, 298 K): δ 13.38 (s, br, 1H), 8.60 (d, J = 5.2 Hz, 1H), 8.22 (s, 1H), 7.84 (d, J = 3.6 Hz, 1H), 7.60 (dd, J = 5.2 Hz, J = 2.0 Hz, 1H), 7.54 (d, J = 8.8 Hz, 2H), 7.42 - 7.41 (m, 2H), 7.09 (d, J = 8.8 Hz, 4H), 6.93 (d, J = 9.2 Hz, 4H), 6.86 (d, J = 8.8 Hz, 2H), 3.99 (t, J = 6.8 Hz, 4H), 1.80 - 1.73 (m, 4H), 1.52 - 1.44 (m, 4H), 1.37 - 1.34 (m, 8H), 0.90 (t, J = 7.0 Hz, 6H). ¹⁹F NMR (376 MHz, d_6 -acetone, 298K): δ -62.58 (s, 3F).

Synthesis of 8

Compound **8** was synthesized according to the procedures as described for **7**, but the reactants were switched to HexylOTPA-B (1.31 g, 2.29 mmol), 4,7-dibromo-2,1,3-benzothidiazole (809 mg, 2.75 mmol) and Pd(PPh₃)₄ (0.05 eq). It was obtained as a

red oil (1.09 g, 72%).

Spectral data of **8**: ¹H NMR (400 MHz, CDCl₃, 298 K): δ 7.87 (d, *J* = 7.6 Hz, 1H), 7.74 (d, *J* = 8.8 Hz, 2H), 7.50 (d, *J* = 7.6 Hz, 1H), 7.12 (d, *J* = 8.4 Hz, 4H), 7.02 (d, *J* = 8.4 Hz, 2H), 6.85 (d, *J* = 8.8 Hz, 4H), 3.94 (t, *J* = 6.4 Hz, 4H), 1.82 - 1.75 (m, 4H), 1.50 - 1.43 (m, 4H), 1.37 - 1.33 (m, 8H), 0.91 (t, *J* = 7.0 Hz, 6H).

Synthesis of 9

A solution of **8** (420 mg, 0.64 mmol), bis(pinacolato)diboron (1.2 g, 0.47 mmol), Pd(dppf)Cl₂ (0.1 eq), KOAc (0.6 g, 6.12 mmol) in 1,4-dioxane (20 mL) was heated at 60 °C overnight. After cooling to RT, the mixture was poured into water, extracted with CH₂Cl₂ and dried over Na₂SO₄. Solvent was removed and the residue was purified using column chromatography to give **9** as a red viscous oil (290 mg, 63%). Spectral data of **9**: ¹H NMR (400 MHz, CDCl₃, 298 K): δ 8.21 (d, *J* = 7.2 Hz, 1H), 7.82 (d, *J* = 8.8 Hz, 2H), 7.64 (d, *J* = 7.2 Hz, 1H), 7.12 (d, *J* = 8.8 Hz, 4H), 7.03 (d, *J* = 8.4 Hz, 2H), 6.85 (d, *J* = 8.8 Hz, 4H), 3.94 (t, *J* = 6.4 Hz, 4H), 1.82 - 1.75 (m, 4H), 1.49 - 1.43 (m, 4H), 1.36 - 1.34 (m, 8H), 0.92 (t, *J* = 6.8 Hz, 6H).

Synthesis of **10**

Compound **10** was synthesized as a black solid (170 mg, 80%) using procedures as described for **7**, starting from **9** (157 mg, 0.22 mmol), **6** (101 mg, 0.22 mmol) and $Pd(PPh_3)_4$ (0.05 eq).

Spectral data of **10**: ¹H NMR (400 MHz, CDCl₃, 298 K): δ 8.62 (d, *J* = 5.2 Hz, 1H), 8.34 (s, 1H), 8.14 (d, *J* = 3.6 Hz, 1H), 7.98 (d, *J* = 7.6 Hz, 1H), 7.83 (d, *J* = 8.4 Hz, 2H), 7.71 - 7.69 (m, 2H), 7.53 (d, *J* = 5.2 Hz, 1H), 7.40 (s, 1H), 7.13 (d, *J* = 8.8 Hz, 4H), 7.05 (d, *J* = 8.8 Hz, 2H), 6.86 (d, *J* = 9.2 Hz, 4H), 5.52 (dd, *J* = 9.6 Hz, *J* = 2.4 Hz, 1H), 4.16 - 4.14 (m, 1H), 3.95 (t, *J* = 6.4 Hz, 4H), 3.76 - 3.70 (m, 1H), 2.72 - 2.65 (m, 1H), 2.21 - 2.17 (m, 1H), 2.07 - 2.03 (m, 1H), 1.82 - 1.63 (m, 7H), 1.51 - 1.44 (m, 4H), 1.37 - 1.33 (m, 8H), 0.92 (t, *J* = 7.2 Hz, 6H). ¹⁹F NMR (376 MHz, CDCl₃, 298K): δ -59.37 (s, 3F).

Synthesis of compound L3H

L3H was synthesized as described for **L2H**, using **10** (160 mg, 0.17 mmol) as the starting material. Yield: 121 mg and 83%.

Spectral data of **L3H**: ¹H NMR (400 MHz, CDCl₃, 298 K): δ 11.71 (s, br, 1H), 8.61 (d, *J* = 5.2 Hz, 1H), 8.10 (d, *J* = 4.0 Hz, 1H), 7.98 (d, *J* = 7.2 Hz, 1H), 7.85 (s, 1H), 7.82 (d, *J* = 8.8 Hz, 2H), 7.70 (d, *J* = 7.6 Hz, 1H), 7.66 (d, *J* = 4.0 Hz, 1H), 7.56 (dd, *J* = 5.6 Hz, *J* = 2.0 Hz, 1H), 7.12 (d, *J* = 8.8 Hz, 4H), 7.07 (s, 1H), 7.04 (d, *J* = 8.8 Hz, 2H), 6.85 (d, *J* = 8.8 Hz, 4H), 3.94 (t, *J* = 6.4 Hz, 4H), 1.81 - 1.74 (m, 4H), 1.48 - 1.42 (m, 4H), 1.36 - 1.32 (m, 8H), 0.90 (t, *J* = 7.0 Hz, 6H). ¹⁹F NMR (376 MHz, CDCl₃, 298K): δ -62.32 (s, 3F).

Synthesis of intermediates Ru1Cl – Ru3Cl

A solution of (tectpy)RuCl₃ (723 mg, 1.1 mmol), **L1H** (269 mg, 1.0 mmol) and KOAc (196 mg, 2.0 mmol) in toluene was heated under reflux for 4h. After cooling to RT, the solvent was removed and the residue was dissolved in CH₂Cl₂, washed with water, dried over Na₂SO₄, and concentrated to dryness. The crude product was purified using column chromatography to give **Ru1Cl** as a black solid (570 mg, 67%). Ru(II) complexes **Ru2Cl** (400 mg, 73%) and **Ru3Cl** (103 mg, 60%) were synthesized using chelates **L2H** and **L3H** under similar condition.

Spectral data of **Ru1Cl**: ¹H NMR (400 MHz, CDCl₃, 298 K): δ 9.88 (d, *J* = 6.0 Hz, 1H), 8.83 (s, 2H), 8.71 (s, 2H), 7.94 (d, *J* = 5.6 Hz, 2H), 7.81 (s, 1H), 7.75 (dd, *J* = 5.8 Hz, *J* = 1.8 Hz, 2H), 7.52 (d, *J* = 4.4 Hz, 1H), 6.74 (s, 1H), 4.64 - 4.59 (m, 2H), 4.48 - 4.42 (m, 4H), 1.59 - 1.54 (m, 12H), 1.42 (t, *J* = 7.2 Hz, 6H). ¹⁹F NMR (376 MHz, CDCl₃, 298K): δ -60.34 (s, 3F).

Spectral data of **Ru2CI**: ¹H NMR (400 MHz, CDCl₃, 298 K): δ 9.93 (d, *J* = 6.0 Hz, 1H), 8.83 (s, 2H), 8.71 (s, 2H), 8.02 (d, *J* = 5.6 Hz, 2H), 7.97 (s, 1H), 7.74 (dd, *J* = 6.0 Hz, *J* = 1.6 Hz, 2H), 7.69 - 7.66 (m, 2H), 7.49 (d, *J* = 8.4 Hz, 1H), 7.30 (d, *J* = 4.0 Hz, 1H), 7.10 (d, *J* = 8.8 Hz, 4H), 6.96 (d, *J* = 8.4 Hz, 2H), 6.86 (d, *J* = 8.8 Hz, 4H), 6.80 (s, 1H), - S9 - 4.63 - 4.58 (m, 2H), 4.48 - 4.42 (m, 4H), 3.95 (t, *J* = 6.6 Hz, 4H), 1.83 - 1.76 (m, 4H), 1.57 (t, *J* = 7.2 Hz, 3H), 1.51 - 1.46 (m, 4H), 1.42 (t, *J* = 7.2 Hz, 6H), 1.38 - 1.33 (m, 8H), 0.92 (t, *J* = 6.8 Hz, 6H). ¹⁹F NMR (376 MHz, CDCl₃, 298K): δ -60.35 (s, 3F).

Spectral data of **Ru3Cl**: ¹H NMR (400 MHz, CDCl₃, 298 K): δ 9.99 (d, *J* = 6.0 Hz, 1H), 8.82 (s, 2H), 8.70 (s, 2H), 8.20 (d, *J* = 4.0 Hz, 1H), 8.07 (s, 1H), 8.05 - 8.02 (m, 3H), 7.86 - 7.82 (m, 3H), 7.76 - 7.72 (m, 4H), 7.13 (d, *J* = 8.8 Hz, 4H), 7.05 (d, *J* = 8.8 Hz, 2H), 6.87 - 6.85 (m, 5H), 4.62 - 4.57 (m, 2H), 4.46 - 4.41 (m, 4H), 3.94 (t, *J* = 6.4 Hz, 4H), 1.82 - 1.74 (m, 4H), 1.56 (t, *J* = 7.2 Hz, 3H), 1.50 - 1.44 (m, 4H), 1.40 (t, *J* = 7.2 Hz, 6H), 1.37 - 1.32 (m, 8H), 0.91 (t, *J* = 7.2 Hz, 6H). ¹⁹F NMR (376 MHz, CDCl₃, 298K): δ -60.35 (s, 3F).

sensitizer	J _{sc} [mA cm ⁻²]	V _{oc} [mV]	FF	η [%]	dye loading [x 10 ⁻⁷ mol cm ⁻ ²]
PRT-tBu ^[a]	12.92	810	0.77	8.09	
	12.83	810	0.76	7.97	1.11
	13.36	800	0.77	8.22	
PRT-tBu ^[b]	14.92	810	0.76	9.21	
	14.67	810	0.76	9.03	1.46
	15.10	800	0.75	9.09	
PRT-tBu ^[c]	16.23	790	0.75	9.68	
	16.40	790	0.75	9.78	2.37
	16.24	780	0.75	9.54	
PRT-ND1 ^[a]	14.24	810	0.74	8.49	
	14.05	800	0.73	8.23	0.72
	14.15	800	0.75	8.44	
PRT-ND1 ^[b]	15.98	790	0.73	9.26	
	15.80	790	0.74	9.24	1.01
	16.08	780	0.73	9.18	
PRT-ND1 ^[c]	16.33	780	0.75	9.50	
	16.24	780	0.75	9.49	1.76
	16.40	770	0.75	9.44	
PRT-ND2 ^[a]	12.36	780	0.73	7.08	
	11.93	780	0.74	6.91	0.75
	13.43	770	0.70	7.28	
	13.84	780	0.74	7.96	
	14.00	780	0.73	7.79	0.30

Table S1. The performances for individual DSCs measured under AM1.5G one sunirradiation.

	14.33	770	0.73	8.06	
	14.70	770	0.74	8.33	
PRT-ND2 ^[c]	15.53	760	0.70	8.22	1.63
	14.91	770	0.73	8.38	

measured under AM1.5G one sun irradiation.							
sensitizer	J _{sc} [mA cm ⁻²]	V _{oc} [mV]	FF	η [%]	Active area		
- Z907	15.60	770	0.755	9.06	0.16		
	13.28	740	0.50	4.91	22.34		
	9.95	740	0.49	3.61	28.40		

Table S2. The performance characteristics for DSCs with commercial Z907 sensitizer,measured under AM1.5G one sun irradiation.

Electrolyte is composed of 1 M DMII, 0.03 M I_2 , 0.05 M LiI, 0.1 M GuNCS, and 0.5 M TBP in AN/VN (85/15).