## **ELECTRONIC SUPPLEMENTARY INFORMATION**

## Design and synthesis of novel organometallic dyes for NiO sensitization and photo-electrochemical applications.

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Synthesis of 5-trimethylsilylethynyl-2-thiophenecarboxylic acid: To a solution of 5-bromo-2thiophenecarboxylic acid (1.0 g, 4.8 mmol, 1 equiv.),  $PdCl_2(PPh_3)_2$  (85 mg, 0.12 mmol, 5%) and CuI (45 mg, 0.24 mmol, 2.5%) in dry THF (20 mL) under inert atmosphere, were added diethylamine (20 mL) and trimethylsilylacetylene (0.75 mL, 5.3 mmol, 1.1 equiv.). The suspension was stirred for 20 h at RT. After evaporation of the solvent, the crude was dissolved in  $CH_2Cl_2$ . The solution was washed with diluted HCl solution, filtered, dried over MgSO4 and evaporated. The crude product was purified on silica gel column chromatography (EtOAc/MeOH, 9:1) to afford 5-trimethylsilylethynyl-2-thiophenecarboxylic acid as a white powder in 50 % yield (0.54 g, 2.4 mmol). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.72 (d, 1H, <sup>3</sup>J<sub>HH</sub> = 4.0 Hz), 7.19 (d, 1H, <sup>3</sup>J<sub>HH</sub> = 4.0 Hz), 0.27 (s, 9H).

Synthesis of 5-ethynyl-2-thiophenecarboxylic acid: To a solution of 5-trimethylsilylethynyl-2-thiophenecarboxylic acid (500 mg, 2.2 mmol, 1 equiv.) in dry MeOH (60 mL) and under inert atmosphere, was added K<sub>2</sub>CO<sub>3</sub> (600 mg, 4.4 mmol, 2 equiv.). The suspension was stirred at RT for 24 h. After concentration of the solution, the reaction mixture was poured into diluted HCl solution and extracted with CH<sub>2</sub>Cl<sub>2</sub>. The organics were further washed with brine, dried over MgSO<sub>4</sub> and evaporated to dryness to afford 5-ethynyl-2-thiophenecarboxylic acid as a white powder in 65 % yield (220 mg, 1.4 mmol). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.73 (d, 1H, <sup>3</sup>J<sub>HH</sub> = 4.0 Hz), 7.24 (d, 1H, <sup>3</sup>J<sub>HH</sub> = 4.0 Hz), 3.49 (s, 1H).

Synthesis of 5-ethynyl-thiophene-2-trimethylsilyl-2-ethanoate (2): To a solution of 5-ethynyl-2-thiophenecarboxylic acid (210 mg, 1.4 mmol, 1 equiv.) in dry DMF (3 mL) under nitrogen atmosphere, HBTU (630 mg, 1.7 mmol, 1.2 equiv.), 2-(trimethylsilyl)ethanol (0.28 mL, 1.9 mmol, 1.4 equiv.) and N,N-diisopropylethylamine (1.2 mL, 6.9 mmol, 5 equiv.) were added sequentially. The solution was stirred at RT for 20 h. After dilution with CH<sub>2</sub>Cl<sub>2</sub> the reaction mixture was washed with saturated aqueous NH<sub>4</sub>Cl solution and water, then dried over MgSO<sub>4</sub> and evaporated to obtain **2** as a white powder in 86 % yield (300 mg, 1.2 mmol). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.62 (d, 1H, <sup>3</sup>J<sub>HH</sub> = 4.0 Hz), 7.21 (d, 1H, <sup>3</sup>J<sub>HH</sub> = 4.0 Hz), 4.39 (m, 2H), 3.44 (s, 1H), 1.10 (m, 2H), 0.08 (s, 9H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  = 161.6, 135.2, 133.4, 132.8, 128.3, 83.7, 76.2, 63.9, 17.4, -1.3.

**Table S1**. TD-DFT validation test of different exchange-correlation density functional models for predicting the vertical excitation energies of **[Ru]1** dye in dichloromethane.

[ <b>Ru</b> ]1 <sup>(a)</sup>	1 <sup>st</sup> excitation (nm)	2 <sup>nd</sup> excitation (nm)
B3LYP	861	550
PBE0	820	525
mPW1PBE	818	524
mPW1PW91	818	524
M06-2X	753	455
CAM-B3LYP	707	448
ωB97X	696	441
LC-@PBE	676	423
Exp.	602	340

(a) Dichloromethane solvent is described via PCM



**Figure S1**. Charge density difference iso-surface plots between excited-  $(S_1)$  and ground-state  $(S_0)$  electron densities of **[Ru]1** (left) and **[Ru]2** (right). The yellow surface represents positive charge density values (*i.e.*, excited electron localization in S1), the cyan surface represents negative charge density values (*i.e.*, hole in the ground-state)

## Single crystal X-Ray crystallography

Table S2 : X-Ray data statistics for compound **4**.

Crystal System	Monoclinic
Space Group	P2 <sub>1</sub> /c
Ζ	4
Unit Cell Parameters a, Å	15.5292(3)
Unit Cell Parameters b, Å	18.0323(5)
Unit Cell Parameters c, Å	27.1454(19)
Unit Cell Parameters α, °	90
Unit Cell Parameters β, °	92.228(7)
Unit Cell Parameters γ, °	90
Temperature, K	123
Volume, Å3	7595.7(6)
FW, g.mol-1	1477.22
ρ, g.cm-3	1.292
λ, Ε	3.499
θ min	6.528
θ max	63.674
Radiation	1.54187
Reflections Measured	38290
Reflections Unique ( $[Fo > 2\sigma Fo]$ )	9556
Parameters/restraints	795/136
GOF	1.127
R1 (I>2σ(I))	00658
wR2 (all data)	0.1734
CCDC#	CCDC 1460734

Data collection was performed at the IECB X-ray facility (UMS3033) on a high flux microfocus Rigaku (MM007, 1.2kW) rotating anode at the copper ka wavelength. The experimental setup is composed of osmic Varimax mirrors and a semi-cylindrical R-Axis spider IP detector. The crystal was mounted on a cryo-loop after quick soaking on Paratone-N oil from Hampton research and flash-frozen at 123K. The diffractometer has a partial chi geometry goniometer allowing omega-scan data collections. The data were processed with the CrystalClear suite version 2.1b25 (1). The crystal structure was solved using direct methods implemented in SHELXT (2) and was refined using SHELXL 2013 version (3). Full-matrix least-squares refinement were performed on F2 for all unique reflections, minimizing w(Fo<sup>2</sup>-Fc<sup>2</sup>), with anisotropic displacement parameters for non-hydrogen atoms. Hydrogen atoms were positioned in idealized positions and refined with a riding model, with Uiso constrained to 1.2 Ueg value of the parent atom (1.5 Ueg when CH3). The positions and isotropic displacement parameters of the remaining hydrogen atoms were refined freely. The RIGU command was used to restrain parts of the molecule as rigid groups and restrain their displacement parameters. The terminal ester group is disordered in this crystal structure and two positions have been modeled. Data statistics are presented in Table S2 and in the cif file CCDC 1460734.

- (1) CrystalClear (Rigaku/MSC, 2006)
- (2) G. M. Sheldrick, Acta Cryst. A 2015, A71, 3-8.
- (3) G. M. Sheldrick, Acta Cryst. A 2008, A64, 112-122.