Supplementary Material (ESI) for Organic and Biomolecular Chemistry

Optoelectronically Mismatched Oligophenylethynyl-Naphthalenediimide SHJ Architectures

Santanu Maity, Rajesh Bhosale, Natalie Banerji, Eric Vauthey, Naomi Sakai*

and Stefan Matile*

Supplementary Information

1. Materials and methods

Reagents for synthesis were purchased from Fluka, Acros and Aldrich. Amino acid derivatives were purchased from Novabiochem and Bachem, HATU from Applied Biosystems, buffers, and salts from Sigma or Fluka-Aldrich. All reactions were performed under N_2 or argon atmosphere. Column chromatography was carried out on silica gel 60 (Fluka, 40-63 μm). Analytical (TLC) was performed on silica gel 60 (Fluka, 0.2 mm) and preparative thin layer chromatography (PTLC) was performed on silica gel GF (Analtech, 1 mm). HPLC was performed using either Jasco HPLC system (PU-980, UV-970, FP-920) or an Agilent 1100 series apparatus with a photo diode array detector. MALDI-TOF was performed on an Axima CFR$^+$ (Shimadzu). UV-Vis spectra were recorded on a JASCO V-650 spectrophotometer equipped with a stirrer and a temperature controller (25 ºC) and are reported as maximal absorption wavelength λ in nm (extinction coefficient ε in $mM^{-1}cm^{-1}$). ^1H spectra were recorded (as indicated) either on a Bruker 300 MHz, 400 MHz or 500 MHz spectrometer and are reported as

chemical shifts (δ) in ppm relative to TMS ($\delta = 0$). Spin multiplicities are reported as a singlet (s), doublet (d), triplet (t), quartet (q) and quintet (quint) with coupling constants (J) given in Hz, or multiplet (m). Broad peaks are marked as br. ^{1}H resonance was assigned with the aid of additional information from 1D & 2D NMR spectra (H, H-COSY, DEPT 135, HSQC and HMBC). Electrochemical measurements were done on an Electrochemical Analyzer with Picoamp booster and Faraday cage (CH Instruments 660C). Photocurrents were measured using a 150 W solar simulator (Newport) and an Electrochemical Analyzer (CH Instruments 660C). The irradiation power was measured using a radiant power energy meter (Newport model 70260).

Abbreviations. DMF: N,N-Dimethylformamide; DTBP: 2, 6-di-*tert*-butylpyridine; *FF*: Fill factor; HATU: N-[(Dimethylamino)-1*H*-1,2,3-triazolo[4,5-b]pyridin-1-ylmethylene]-N-methylmethanammonium hexafluorophosphate N-oxide; IPCE: Incident photon to current conversion efficiency; LBL: layer-by-layer assembly; NDI: 1,4,5,8-Naphthalenediimide; OPE: Oligophenylethynyl; POP: *p*-Oligophenyl; rt: Room temperature; TEA: Triethylamine; TEOA: Triethanolamine; TFA: Trifluoroacetic acid; TFE: 2,2,2-Trifluoroethanol; Z = Benzyloxycarbonyl.

2. Synthesis

OPE 7. This compound was prepared from starting materials **8**-**10** following previously reported procedures. [S1]

NDI 11. This compound was prepared following previously reported procedures. [S2]

OPE-B 12. A solution of freshly prepared **7** (3 mg, 2.5 μmol), **11** (45 mg, 73.9 μmol), and HATU (13.5 mg, 35.6 μmol) in freshly distilled DMF (1.5 ml) was treated with TEA (28 μl, 0.2 mmol) and DTBP (67 μl, 0.3 mmol). The reaction was stirred for 20 h at rt. DMF was removed under vacuum, and solid-liquid extraction was performed with methanol. The crude product (50 mg) was further purified by column chromatography (CH_2Cl_2/MeOH 90:10) and PTLC (CH_2Cl_2/MeOH 95:5) to yield analytically pure (HPLC, YMC-Pack SIL 250 x 10 mm, CH_2Cl_2/MeOH 90:10, 2 ml / min, R_t = 6.69 min) **12** (5 mg, 25%) as a blue solid. ^{1}H NMR (400 MHz, $CDCl_3$/CD_3OD 10:1): 8.12 - 7.93 (m, 22H), 7.50 - 7.21 (m, 46H), 7.22 - 6.34 (m, 14H), 5.80 - 5.60 (m, 13H), 5.22 - 5.00 (m, 20H), 4.81 - 4.32 (m, 27H), 4.21 - 3.91 (m, 23H), 3.82 - 3.51 (m, 23H), 3.22 - 3.14 (m, 18H), 2.50 - 2.10 (m, 24H), 1.91 - 1.34 (m, 215H); MS (MALDI, DITH): 7898 (100, $[M+H])^+$.

OPE-B 5. A solution of **12** (2 mg, 0.25 μmol), thioanisol (62 mg, 0.5 mmol), pentamethylbenzene (74 mg, 0.5 mmol) in TFA (2 ml) was stirred for 1 h at 50 °C. Cooled to rt, the solvents were removed under nitrogen flow. The same procedure was repeated once more. The crude product was purified by sequential wash with DCM, Acetonitrile and Ether to yield analytically pure (RP-HPLC, Nucleosil 100-7 c18 250 x 8 mm, MeOH (with 1% TFA) / H_2O 90:10, 1 ml / min, R_t = 6.55 min) **5** (4.6 mg, quantitative) as blue solid. ^{1}H NMR (400 MHz, CD_3OD): 8.05 - 7.65 (m, 32H), 7.76 - 6.78 (m, 10H), 5.61 - 5.44 (m, 13H), 5.27 - 4.70 (m, 25H), 4.71 - 3.82 (m, 67H), 3.84 - 3.48 (m, 17H), 3.12 - 2.92 (m, 27H), 2.65 - 1.92 (m, 22H), 1.85 - 0.82 (m, 242H); MS (MALDI, DITH): 6554 (100, $[M+H]^+$).

NDI 13. This compound was prepared following previously reported procedures. [S3]

OPE-B 14. A solution of freshly prepared **7** (3 mg, 2.5 μmol), **13** (60 mg, 90 μmol), HATU (13 mg, 35 μmol) in freshly distilled DMF (1.5 ml) was treated with TEA (28 μl, 0.2 mmol) and DTBP (67 μl, 0.3 mmol). The reaction was stirred for 20 h at rt. DMF was removed under vacuum and solid-liquid extraction was performed with methanol. The crude product (60 mg) was further purified by solid column chromatography (CH_2Cl_2/MeOH 90:10), and PTLC (CH_2Cl_2/MeOH 90:10) to yield analytically pure (HPLC, YMC-Pack SIL 250 x 4.6 mm, CH_2Cl_2/MeOH 95:5, 1ml / min, R_t = 7.73 min) **14** (7 mg, 35%) as a blue solid. ^{1}H NMR (400 MHz, $CDCl_3$/CD_3OD 4:1): 8.12 - 7.56 (m, 24H), 7.15 - 6.50 (m, 12H), 5.72 - 5.50 (m, 10H), 4.77 - 4.20 (m, 26H), 4.00 - 3.35 (m, 53H), 2.67 - 2.08 (m, 42H), 2.01 - 1.74 (m, 45H), 1.65 - 1.00 (m, 224H); (MALDI, DITH): 7146 (100, $[M+Na]^+$).

OPE-B 6. A solution of **14** (2.0 mg, 0.3 μmol) in TFA: CH_2Cl_2 (2 ml, 1:1) was stirred for 1 h at rt. TFA was removed by nitrogen flow. The same procedure was repeated once more. The crude product was purified by sequential wash with DCM, acetonitrile and ether to yield **6** (1.8 mg, quantitative). ^{1}H NMR (400 MHz, $CDCl_3$/TFA 1:1): 8.50 - 8.90 (m, 25H), 6.12 - 5.91 (m, 10H), 4.61 - 4.18 (m, 50H), 3.41 - 3.23 (m, 20H), 2.95 - 2.42 (m, 40H), 1.85 - 1.65 (m, 60H); MS (MALDI, DITH): 6577 (100, $[M+NH_4]^+$), 6591 (80, $[M+K]^+$).

OPE-N 4. This compound was prepared following previously reported procedures. [S1]

POP-N 1. This compound was prepared following previously reported procedures.[S2]

POP-B 2. This compound was prepared following previously reported procedures.[S1]

POP-B 3. This compound was prepared following previously reported procedures.[S5]

3. Conformational studies

Absorption spectra of OPE-B **6** (45 μM) were recorded in water-TFE with different solvent ratio and pH as a variable. Absorption spectra of OPE-B **6** with variable solvent ratio were measured in water-TFE (10:0, 9:1, 7:3, 6:4, 5:5, 3:7, 1:9), pH = 8.4, 20 mM buffer (TEOA). Absorption spectra of OPE-B **6** (45 μM) with variable pH were measured in water-TFE (9:1), at pH 3, 4, 5, 6, 7, 8, 9 and 10 with 20 mM TEOA (pH = 3 to 7) or 20 mM MES (pH = 8 to 10).

4. Photocurrent generation

Gold electrodes. Gold electrodes were prepared as reported in reference S4: Gold-coated glass slides (22 x 22 mm^2) were purchased from Mivitec GmbH, Analytical μ-Systems (Germany). Before use, the plates were cut in half (~ 1 x 2 cm^2), and cleaned using 'piranha' solution (H_2SO_4 / 30 % H_2O_2 3 / 1; 35 °C for 5 min).[S5] *Caution: piranha solution reacts violently with organic compounds. It should be handled with extreme care.* After the treatment with piranha solution, the plates were thoroughly rinsed with water and EtOH, and used immediately.

Zipper initiation. Zipper assembly was initiated as reported in reference S1: The cleaned gold plates were immersed in the solution of the anionic initiator **4** (0.3 mM) in a 1:0.4 mixture of DMF:water for 4 days. The obtained Au-**4** electrodes were tested for defects using the standard

procedure in which reduction-oxidation of $K_3Fe(CN)_6$ (2 mM in 1 M aqueous KNO_3) was measured by cyclic voltammetry using Au-**4** as working electrode (Figure S4A)[S3, S4]. The absence of redox wave confirmed the absence of large uncovered areas on the Au electrode.[S1]

LBL initiation. For LBL assembly, the gold electrodes were coated with lipoic acid. Namely, the cleaned gold plates were immersed in the solution of lipoic acid **15** (10 mM) in 0.5 mM sodium phosphate, 0.5 M NaCl, 50% aqueous TFE buffer pH 7, for 1 day. The obtained Au-**15** electrodes were tested for defects as described above.

Propagation. Coated gold electrodes Au-**4** or Au-**15** were immersed in the solution of *cationic* OPE-B **5** (10 μM) in a mixture of water (83%) and TFE (17%) with 0.5 mM sodium phosphate, 0.1 M NaCl buffer (pH 7) for two days, unless stated. The plate was rinsed repeatedly with bidistilled water and TFE, and the photocurrent of the resulting plate was recorded. The obtained bilayer coated plate was similarly treated with *anionic* OPE-B **6** to give the trilayer coated plate. Multilayers were obtained by repeating these sequences of depositions.

Photocurrent measurements. Coated gold electrodes were used as a working electrode with a Pt wire as a counter electrode and Ag/AgCl as a reference electrode. The electrodes were immersed in a deaerated (by bubbling N_2 gas) aqueous solution of TEOA (50 mM) and Na_2SO_4 (0.1 M) and irradiated with a solar simulator (area of irradiation: a = ~0.7 cm^2). Changes in current upon on-off switching of irradiations (20 seconds each) were measured at +0.4 V *vs* Ag/AgCl unless stated. The power of irradiation was 66 mW cm^{-2}.

***I-V* measurements**. Short circuit current (I_{sc}) and open circuit voltage (V_{oc}) of zipper and

LBL assemblies were determined by *I-V* measurements of Au-**4**-(**5**-**6**-)$_4$-**5**, Au-**15**-(**5**-**6**-)$_4$-**5** (Figure 6). Experimental conditions were as described in the above "photocurrent measurements", but with 87 mW cm^{-2} of irradiation. Fill factors (*FF*) were calculated from the maximum power (P_m), I_{sc} and V_{oc} using equation (S1)[S6]

$$FF = P_m / I_{sc}\, V_{oc} \qquad \text{(S1)}.$$

Action spectra. Photocurrent densities ($J_{sc} = I_{sc} / a$) were measured at 0 V *vs* Ag/AgCl upon excitation by monochromatic light (150 W Xe lamp with Oriel 1/8 m monochromator) (Figure 7). The obtained current densities were converted into incident photon to current conversion efficiencies (IPCEs) by using the equation (S2).[S1]

$$\text{IPCE} = 1240 / \lambda\ (\text{nm}) \times J_{sc} / P_{in} \qquad \text{(S2)}$$

5. Supplementary references

(S1) R. Bhosale, A. Perez-Velasco, V. Ravikumar, R. S. K. Kishore, O. Kel, A. Gomez-Casado, P. Jonkheijm, J. Huskens, P. Maroni, M. Borkovec, T. Sawada, E. Vauthey, N. Sakai and S. Matile, *Angew. Chem. Int. Ed.*, 2009, **48**, 6461-6464.

(S2) R. S. K. Kishore, V. Ravikumar, G. Bernardinelli, N. Sakai and S. Matile, *J. Org. Chem.*, 2008, **73**, 738-740.

(S3) M. Lista, N. Sakai and S. Matile, *Supramol. Chem.*, 2009, **21**, 238-244.

(S4) N. Sakai, A. L. Sisson, T. Bürgi and S. Matile, *J. Am. Chem. Soc.*, 2007, **129**, 15758-15759.

(S5) M. Twardowski and R. Nuzzo, *Langmuir*, 2002, **18**, 5529-5538.

(S6) B. C. Thompson and J. M. J. Fréchet, *Angew. Chem. Int. Ed.*, 2008, **47**, 58-77.