

Supporting Information

Molecular Engineering of D- π -A Type of Blue-Colored Dyes for Highly Efficient Solid State Dye-Sensitized Solar Cells through Co-Sensitization

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1 Photovoltaic Parameters

Table S1. The parameters of performance of ssDSSCs based on different dye ratios.

Dye	J_{sc} [mA cm^{-2}]	V_{oc} [mV]	FF	PCE
D35:DBLue (1:0.5)	10.58	875	0.67	6.2%
D35:DBLue (1:1)	12.41	880	0.67	7.3%
D35:DBLue (1:2)	10.88	840	0.7	6.4%
D35:MKA16 (2:1)	11.86	855	0.68	6.9%
D35:MKA16 (1:1)	12.85	850	0.69	7.5%
D35:MKA16 (1:2)	12.17	845	0.69	7.1%

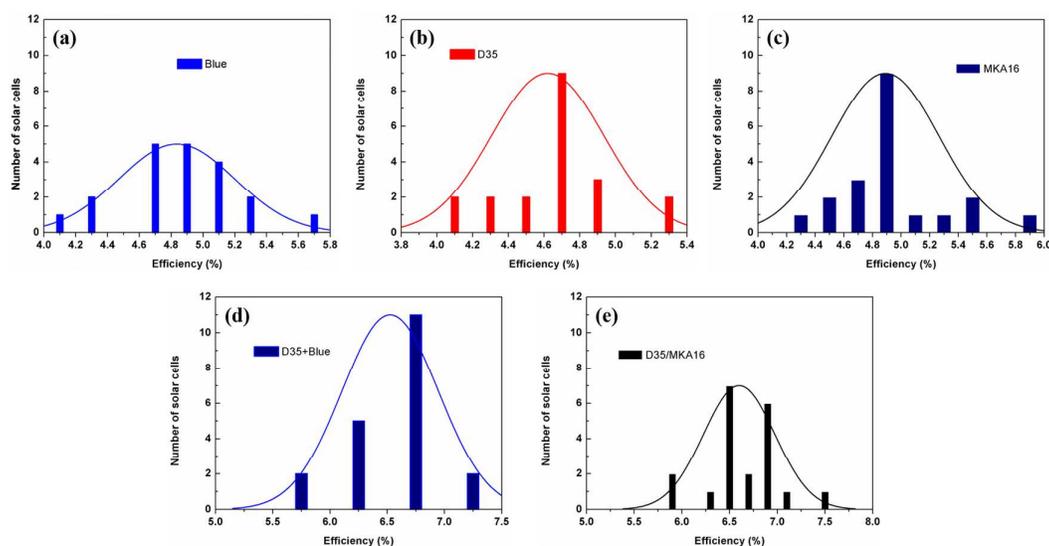


Figure S1. Histogram of efficiency of ssDSSCs based on different dyes. (a) DBLue, (b) D35 (c) MKA16 (d) D35/DBLue and (e) D35/MKA16

2 Experimental section and computational details

2.1 Chemical used

All chemicals came from Sigma-Aldrich company unless otherwise indicated. The dye D35, DBLue and MKA16 were obtained from Dyenamo AB.

2.2 UV-Visible absorption and photoluminescence

UV-Visible absorption spectra were recorded using a Lambda 750 UV-Vis spectrophotometer as described previously¹. The emission spectra were recorded using a Cary Eclipse fluorescence spectrophotometer.

2.3 Photoinduced absorption spectroscopy

The solid-state solar cell substrates for in photoinduced absorption (PIA) measurements were prepared as described above without the final Ag contact layer. PIA spectra were recorded on a specially home-made setup². The 20W tungsten-halogen lamp was used to generate the white probe light. In case of excitation light, a square-wave modulated (on/off) blue light source (Lasermate GML532-100FLE, 460 nm) was performed. The transmitted probe light was focused onto a monochromator and detected by a UV-enhanced silicon and germanium photodiode detector. The light intensity of 6.1 mWcm^{-2} and 9.33 Hz modulation frequency were used for the blue LED light excitation.

2.4 Computational methods

Density functional theory calculations (DFT) were performed to generate the relaxed geometries of the molecules under study. Optimization and single point energy calculations were performed using the B3LYP functional and 6-31G* basis sets for all atoms. The geometrical optimizations were performed without any symmetry constraints. All reported calculations were carried out by means of Gaussian 09.³ The absorption spectra and excitation energies were calculated by time-dependent density functional theory (TD-DFT) using the cam-b3lyp/6-311+G functional. The solvent effects were taken into consideration using the polarizable continuum model (PCM). The reorganization energy for the charge transfer (CT) consists of both internal and external contributions. For most crystals formed by organic molecules, the external contribution is small and can be neglected. The equation for calculating the internal reorganization energy λ is determined by the Nelson four-point method:⁴ $\lambda = E_{+}^{*} - E_{+} + E_{+}^{*} - E_{+}^{\square}$ where E_{+}^{\square} is the energy of the neutral molecule in the cation symmetry, and the E_{+} is total energy of the optimized cationic molecule; the E_{+}^{\square} is the total energy of the cationic molecule in the neutral symmetry, and E is the total energy of the optimized neutral molecule.

2.5 Device fabrication and characterization

Fluorine-doped SnO₂ (FTO) glass substrates were dipped into a Zn-HCl solution in order to etch the desired electrode pattern. After this initial step, the substrates were cleaned in an ultrasonic bath in the following order: deionized water (15 min), acetone (30 min), and ethanol (30 min). A spray pyrolysis deposition (SPD) technique was applied to obtain a compact layer of TiO₂ as blocking layer on top of the FTO substrate (0.2 M Ti-isopropoxide and 2M acetylacetone in isopropanol solution, and a 10-spray cycle was used). Afterwards, a TiO₂ paste was deposited onto the compact layer of TiO₂ using a

screen-printing method. After sintering on a hotplate at 500°C for 30 min, the substrate was post-treated by immersing into a solution of 0.2 M aqueous TiCl_4 at 70°C for 30 min. Then, the substrates were rinsed with deionized water and ethanol, and subsequently annealed on a hotplate at 500°C for another 30 min. After being cooled to 90°C, the hot TiO_2 film was immersed into a dye bath for 18h. The dye bath solution in this work was 0.2 mM of dye in a mixed solvent of tert-butanol and acetonitrile (1:1). After the sensitization step, the electrodes were rinsed with ethanol and dried in a dry N_2 gas flow. The surfaces of the dried substrates were covered by solution of the HTM solution also containing additives, and then spin-coated for 30 s at 2000 rpm to form a uniform HTM layer. Afterwards, a 200 nm thick Ag layer was deposited on the top of HTM layer by thermal evaporation in a vacuum chamber (Leica EM MED020). Current-voltage characteristics of the ssDSSCs were studied under 100 mW cm^{-2} (AM 1.5) radiation using a Keithley Model 2400 source meter. The light source was calibrated by a certified reference solar cell (Fraunhofer ISE). A black mask with an aperture area of 0.126 cm^2 was placed on the top of the cell during the measurements. The electron lifetime data were recorded through monitoring photovoltaic transients at different light intensities by applying a small square-wave modulation to a base light intensity. The photovoltaic response was fitted using first-order kinetics in order to obtain the time constants. Incident photon-to-current conversion efficiency (IPCE) spectra were recorded by a computer-controlled setup comprised of a xenon lamp (Spectral Products ASB-XE-175), a monochromator (Spectral Products CM110) and a Keithley multimeter (Model 2700), calibrated by a certified reference solar cell (Fraunhofer ISE).

2.6 Electrochemistry

For the characterization of the redox behaviour of the dye molecules and HTMs, a three-electrode electrochemical cell was used for the cyclic voltammetry experiments. Whereas, the FTO/ TiO_2 /dye and FTO/ TiO_2 /HTMs layer were used as working electrode when monitoring the redox behaviour of the dye molecules and HTMs on the TiO_2 film, and the supporting electrolyte are 0.1 M $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ in acetonitrile and the ionic liquid 1-Methyl-3-propylimidazolium bis(trifluoromethylsulfonyl)imide, respectively. In all cases, stainless steel was used as counter electrode with an area of 3 cm^2 . The reference electrode was in all cases Ag/AgCl/2M LiCl in ethanol; a salt bridge electrolyte was interposed between working and reference electrode, containing 0.1 M $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ in acetonitrile or ionic liquid depending on the working electrode solvent. For experiments in above electrolyte, the reference electrode was calibrated with ferrocene in the same electrolyte; all potentials are reported vs. SHE.

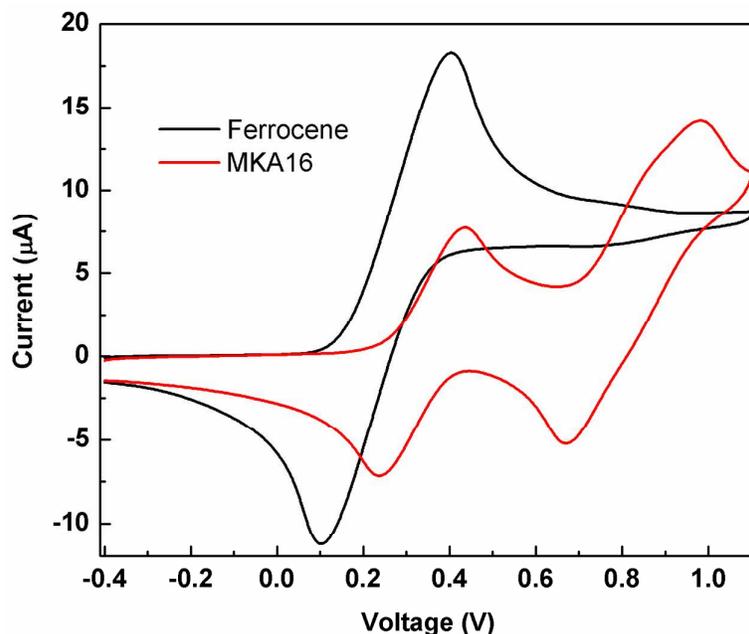


Figure S2. Cyclic voltammetry of MKA16.

2.7 Dye load

Dye films were prepared according to the procedure described in the device fabrication. Two films were used for each measurement. Complete desorption was achieved using a solution of 0.05 M tetramethylammonium hydroxide in acetonitrile. The dye loading was calculated by comparing the absorbance of dye desorption solution to those of the reference D35, DBLue and MKA16 dye solutions both with a fixed concentration of 2×10^{-5} M.

2.8 Synthesis methods

General Experimental: ^1H and ^{13}C NMR spectra were recorded on a Bruker 500 MHz instrument by using the residual signals $\delta = 2.05$, 29.84, and 206.26 ppm from acetone d-6, as internal references for ^1H and ^{13}C respectively. Chemicals used in the synthesis were purchased from Sigma-Aldrich unless otherwise specified. Commercially available reactants were used without further purification unless otherwise noted. Flash chromatography was performed using silica gel 60 Å (35-63 μm). All eluent ratios are given on v/v-basis.

The MKA16 sensitizer was based on the MKA253 donor published by our group in 2015 (10.1039/C4TA05774K) and the DPP linker published by Yum et.al (DOI: 10.1038/srep02446) with the exempt of the octyl chain replacing the ethylhexyl chain in the original structure. The two parts were connected using a Suzuki coupling reaction with XPhos Pd G2 as the Pd catalyst and aqueous solution of K_3PO_4 as the base. The last reaction was the commonly used Knoevenagel condensation with cyanoacetic acid with piperidine as base/catalyst.

5-(4-(4-(5-(4-(bis(5,7-dibutoxy-9,9-dimethyl-9H-fluoren-2-yl)amino)phenyl)thiophen-2-yl)-2,5-dioctyl-3,6-dioxo-2,3,5,6-tetrahydropyrrolo[3,4-c]pyrrol-1-yl)phenyl)furan-2-carbaldehyde (2). 1 (1.0 g, 1.12 mmol), **A** (721 mg, 1.04 mmol) and XPhos Pd G2 (44 mg, 56 μ mol) were dissolved in 30 ml THF. The solution was degassed with nitrogen for 10 min and 9 ml of an aqueous solution of K_3PO_4 (0.5 M, 4.50 mmol) was added. The reaction mixture was stirred at room temperature for 10 min and then kept at 40°C overnight. The solution was extracted with water/diethyleter and the combined organic fractions were run through a short silica plug to remove the black residue. The solvent was evaporated and precipitated in MeOH. The precipitate was filtered and washed with excess MeOH to yield 958 mg of the product as a red solid. NMR showed that a small amount of **1** was still contaminating the product. However since the NMR only showed a single aldehyde peak, the synthesis continued without further purification.

(E)-3-(5-(4-(4-(5-(4-(bis(5,7-dibutoxy-9,9-dimethyl-9H-fluoren-2-yl)amino)phenyl)thiophen-2-yl)-2,5-dioctyl-3,6-dioxo-2,3,5,6-tetrahydropyrrolo[3,4-c]pyrrol-1-yl)phenyl)furan-2-yl)-2-cyanoacrylic acid (MKA16). 2 (crude), (958 mg, 696 μ mol), cyanoacetic acid (177 mg, 2.09 mmol) and piperidine (275 μ l, 2.78 mmol) were dissolved in 35 ml chloroform and refluxed overnight. The solvent was evaporated and the product was purified through flash chromatography using DCM/EtOAc/TEA (6:1:1%) \rightarrow DCM/EtOAc/formic acid (1:1:1%). The product fractions were combined and extracted with water to get rid of the formic acid. Evaporation of the solvents gave 707 mg (yield 70 %) of the product as a black solid. 1H NMR (500 MHz, Acetone- d_6) δ 9.18 (d, J = 4.2 Hz, 1H), 8.18 – 8.06 (m, 5H), 7.92 (d, J = 8.2 Hz, 2H), 7.74 – 7.68 (m, 2H), 7.64 (d, J = 4.2 Hz, 1H), 7.58 (d, J = 3.8 Hz, 1H), 7.42 (d, J = 3.8 Hz, 1H), 7.31 (d, J = 2.1 Hz, 2H), 7.15 – 7.06 (m, 4H), 6.71 (d, J = 2.0 Hz, 2H), 6.53 (d, J = 2.0 Hz, 2H), 4.17 (t, J = 6.3 Hz, 4H), 4.07 (t, J = 6.6 Hz, 6H), 3.97 (t, J = 7.4 Hz, 2H), 1.95 – 1.86 (m, 8H), 1.83 – 1.72 (m, 8H), 1.68 – 1.58 (m, 6H), 1.58 – 1.48 (m, 4H), 1.44 – 1.34 (m, 16H), 1.33 – 1.12 (m, 16H), 1.05 – 0.95 (m, 14H), 0.85 – 0.77 (m, 6H); ^{13}C NMR (126 MHz, Acetone) δ 206.25, 206.09, 205.93, 205.38, 203.88, 163.92, 162.28, 161.48, 157.53, 156.58, 155.23, 152.18, 150.44, 149.59, 145.46, 144.63, 135.91, 130.41, 127.83, 126.14, 124.97, 124.02, 122.30, 120.15, 111.84, 101.24, 98.78, 68.58, 68.38, 48.01, 32.54, 32.50, 32.27, 30.59, 30.49, 30.40, 30.34, 30.30, 30.24, 30.15, 30.09, 29.99, 29.94, 29.92, 29.84, 29.78, 29.69, 29.64, 29.53, 29.42, 29.38, 27.93, 27.47, 27.43, 27.32, 23.29, 20.21, 19.99, 14.40, 14.35, 14.18.

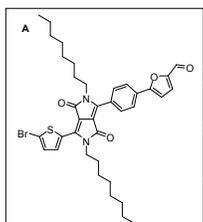
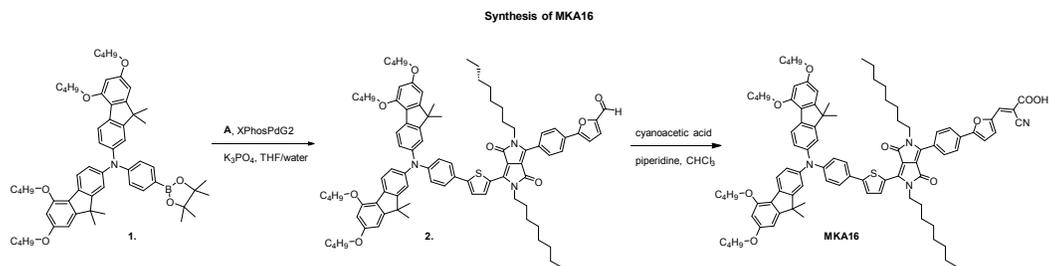
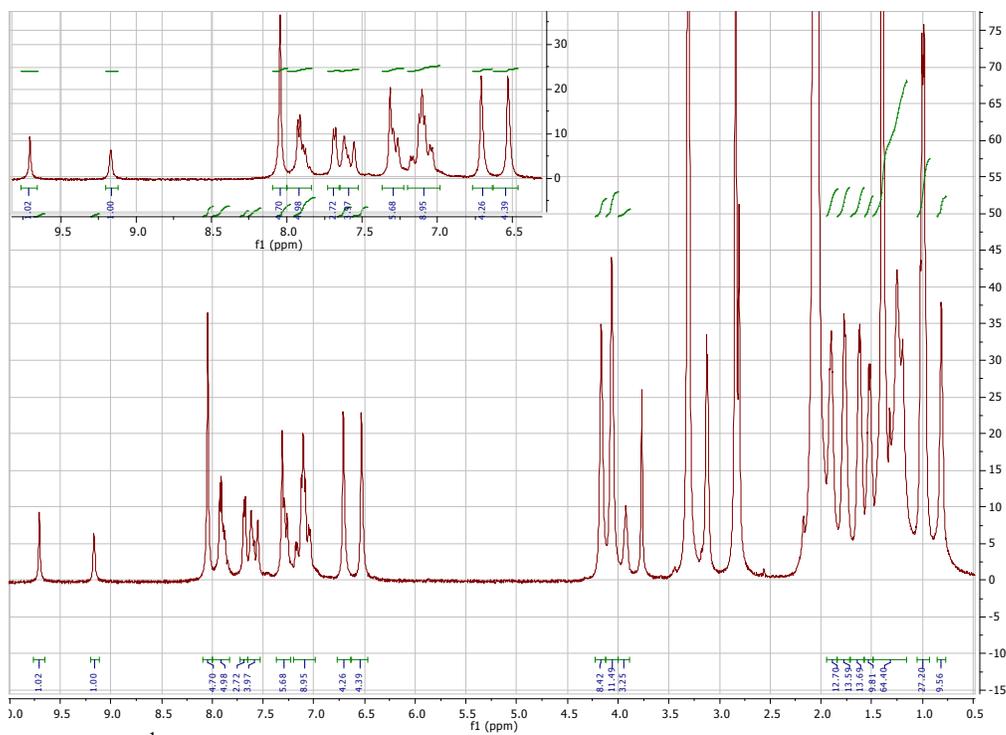


Figure S3. Synthesis route of **MKA16**.



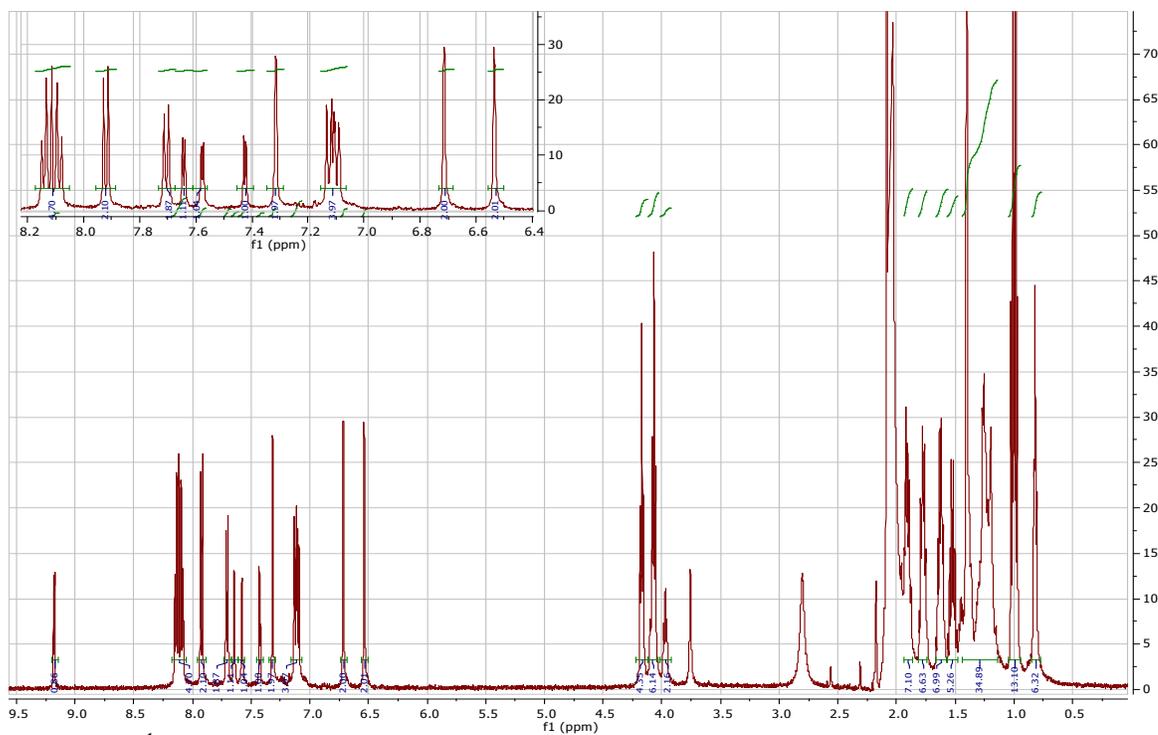


Figure S5. ^1H NMR of MKA16.

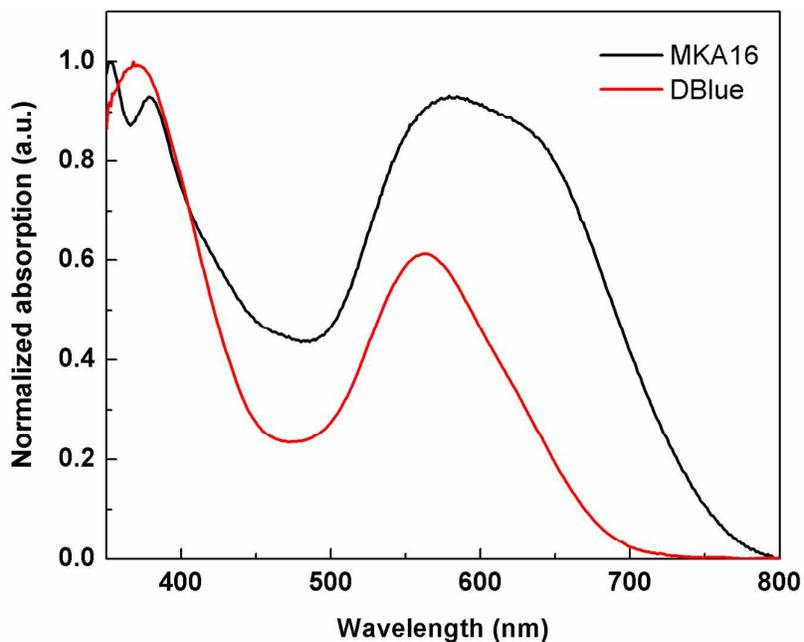


Figure S6. Normalized absorption spectra of MKA16 and Dyenamo Blue on TiO_2 films.

References

1. Liu, P.; Gardner, J. M.; Kloo, L., Solution Processable, Cross-Linked Sulfur Polymers as Solid Electrolytes in Dye-Sensitized Solar Cells. *Chem. Commun.* **2015**, *51*, 14660-14662.

2. Cappel, U. B.; Feldt, S. M.; Schöneboom, J.; Hagfeldt, A.; Boschloo, G., The Influence of Local Electric Fields on Photoinduced Absorption in Dye-Sensitized Solar Cells. *Journal of the American Chemical Society* **2010**, *132*, 9096-9101.
3. Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J., Gaussian-09 Revision D.01.
4. Nelsen, S. F.; Blackstock, S. C.; Kim, Y., Estimation of Inner Shell Marcus Terms for Amino Nitrogen Compounds by Molecular Orbital Calculations. *Journal of the American Chemical Society* **1987**, *109*, 677-682.