Supporting Information

# Saddle-like, $\pi$ -Conjugated, Cyclooctatetrathiophene-Based, Hole-Transporting Material for Perovskites Solar Cells

Javier Urieta-Mora,<sup>a,b</sup> Inés García-Benito<sup>,c</sup> Iwan Zimmermann,<sup>c</sup> Juan Aragó,<sup>d</sup> Joaquín Calbo,<sup>d</sup> Giulia Grancini,<sup>c</sup> Agustín Molina-Ontoria,<sup>b</sup>\* Enrique Ortí,<sup>d</sup>\* Nazario Martín,<sup>a,b</sup>\* Mohammad Khaja Nazeeruddin<sup>c</sup>\*

<sup>a</sup> Departamento Química Orgánica, Facultad C. C. Químicas, Universidad Complutense de Madrid, Av. Complutense s/n, 28040 Madrid (Spain), Homepage: http://www.ucm.es/info/fullerene/. E-mail: <u>nazmar@ucm.es</u>

<sup>b</sup> IMDEA-Nanociencia, C/ Faraday 9, Ciudad Universitaria de Cantoblanco, 28049 Madrid, Spain. E-mail: Agustin.molina@imdea.org

<sup>c</sup> Group for Molecular Engineering of Functional Materials and Laboratory for Photonics and Interfaces EPFL VALAIS, CH-1951 Sion, Switzerland. E-mail: mdkhaja.nazeeruddin@epfl.ch.

<sup>d</sup> Instituto de Ciencia Molecular, Universidad de Valencia, Catedrático José Beltrán 2, 46980 Paterna, Spain, E-mail: <u>enrique.orti@uv.es</u>

### **1. Experimental Section**

General Methods. Chemicals and reagents were purchased from commercial suppliers and used as received. All solvents were dried according to standard procedures. Air-sensitive reactions were carried out under nitrogen atmosphere. The device preparation was done in a glovebox under nitrogen atmosphere. Flash chromatography was performed using silica gel (Merck, Kieselgel 60, 230-240 mesh or Scharlau 60, 230-240 mesh). Analytical thin layer chromatography (TLC) was performed using aluminium-coated Merck Kieselgel 60 F254 plates. NMR spectra were recorded on a Bruker Advance 300 (1H: 400 MHz; 13C: 101 MHz) spectrometer at 298 K using partially deuterated solvents as internal standards. Coupling constants (J) are denoted in Hz and chemical shifts ( $\delta$ ) in ppm. Multiplicities are denoted as follows: s = singlet, d = doublet, t = triplet, m = multiplet. FT-IR spectra were recorded on a Bruker Tensor 27 (ATR device) spectrometer. UV-Vis spectra were recorded in a Varian Cary 50 spectrophotometer. Mass spectra matrix-assisted laser desorption ionization (coupled to a time-of-flight analyzer) experiments (MALDI-TOF) were recorded on a MAT 95 thermo spectrometer and a Bruker REFLEX spectrometer, respectively. Cyclic voltammetry (CV) experiments were conducted in 0.1 M solutions of TBAPF<sub>6</sub> in DCM. Glassy carbon electrode was used as a working electrode and platinum wires were used as counter and reference electrodes. Before each measurement, solution was deoxygenated with N<sub>2</sub>. Ferrocene was added as an internal standard; its oxidation potential in DCM was positioned at 0.7 V vs. NHE. HTM oxidation potential were recalculated in reference to NHE. Thermogravimetric analysis (TGA) was performed using a TA Instruments TGAQ500 with a ramp of 10 °C/min under  $N_2$  from 100 to 1000 °C. Differential scanning calorimetry (DSC) was run on a Discovery DSC from TA instruments. Three cycles were recorded under nitrogen, heating (until 400 °C) and cooling (50 °C) at 20 °C/min of scanning rate.

### 2. Synthetic details and characterization

Compounds  $1^1$  and  $3^2$  were prepared according to previously reported synthetic procedures and showed identical spectroscopic properties to those reported therein.



Scheme S1. Synthetic methodology for the preparation of CoTh-TTPA

#### **Compound 2**

Compounds **2** was prepared according to a modified synthetic procedure reported by Wang *et al.*<sup>3</sup> Compound **1** (1 g, 2.13 mmol) placed in a 100-mL round-bottomed flask and dissolved in anhydrous  $Et_2O$  (40 mL). After the solution was cooled at



-78 °C, a solution of *n*-BuLi (2.5 M, 2.0 mL, 4.9 mmol) was slowly added and then stirred for 1 h. After that, CuCl<sub>2</sub> (850 mg, 6.3 mmol) was added with a N<sub>2</sub> flow and the reaction was stirred overnight at r.t. Then, the mixture was quenched with water and extracted with Et<sub>2</sub>O. The combined organic extracts were dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated in vacuo. The crude was purified by flash column chromatography (hexane) to afford **2** (63%). This compound showed identical spectroscopic properties to those reported in reference 3.

#### **CoTh-TTPA**

A solution of **3** (100 mg, 0.16 mmol), 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-*N*,*N*-bis(4-methoxyphenyl)aniline (335 mg, 0.77 mmol), K<sub>3</sub>PO<sub>4</sub> (790 mg, 3.73 mmol) and Pd(PPh<sub>3</sub>)<sub>4</sub> (36 mg, 0.03 mmol) in DMF (10 mL) was degassed for 30 minutes under nitrogen. The reaction was heated at 100 °C for 3 hours. The mixture was cooled to room temperature and water was added to the reaction. The resulting precipitate was filtered and washed with water and methanol. The solid was then



dissolved in chloroform and dried over sodium sulfate. The solvent was removed under reduced pressure and the crude product was purified by flash column chromatography (silica gel, CH<sub>2</sub>Cl<sub>2</sub>) to afford **CoTh-TTPA** as a bright orange solid (187 mg, 0.12 mmol), yield 78%. <sup>1</sup>H NMR (400 MHz, THF- $d_8$ )  $\delta$ /ppm: 7.40 (m, 8H), 7.20 (s, 4H), 7.04 (m, 16H), 6.85 (m, 24H), 3.75 (s, 24H);

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$ /ppm: 167, 159, 156, 151, 148, 140, 137, 136, 135, 130, 125, 65; FTIR (neat): 3036, 2948, 2832, 1603, 1497, 1462, 1234, 1033, 823 cm<sup>-1</sup> HRMS calcd for C<sub>96</sub>H<sub>76</sub>N<sub>4</sub>O<sub>8</sub>S<sub>4</sub> [M<sup>+</sup>] 1540.45; found 1540.6540.

### **3.** Computational Details

Quantum-chemical calculations were carried out with the Gaussian 16 (revision A.03) software package.<sup>4</sup> All the calculations were performed within the density functional theory (DFT) framework using the B3LYP functional<sup>5</sup> and the 6-31G\*\* basis set.<sup>6</sup> Solvent effects were considered within the self-consistent reaction field (SCRF) theory by using the polarized continuum model (PCM) approach.<sup>7</sup>  $C_2$ -symmetry constraints were imposed during the optimization of CoTh-TTPA and its CoTh central unit. The TPA substituent and the spiro-OMeTAD reference molecule were also optimized under  $C_2$  symmetry. Vertical electronic transition energies to the lowest-energy singlet excited states were computed for CoTh-TTPA by using the time-dependent DFT (TDDFT) approach.<sup>8</sup> The lowest 80 singlet excited states were calculated at the B3LYP/6-31G\*\* level using the ground-state optimized geometry. Reorganization energies ( $\lambda$ ) were computed in gas phase by fully optimizing the geometries of the radical cations of **CoTh-TTPA**, its core, the TPA unit and the spiro-OMeTAD molecule; the evaluation process of  $\lambda$  is explained below. Radical cations were treated as open-shell systems and computed within the spin-unrestricted DFT approximation at the UB3LYP/6-31G\*\* level in the presence of CH<sub>2</sub>Cl<sub>2</sub>. Additionally, dication, trication and tetracation species were also computed in CH<sub>2</sub>Cl<sub>2</sub>. Molecular orbitals were plotted using the Chemcraft 1.6 software with isovalue contours of  $\pm 0.03$  a.u.<sup>9</sup>

Figure S1 shows the B3LYP/6-31G\*\*-optimized structure calculated for both the CoTh core and the **CoTh-TTPA** HTM. Both compounds share a saddle-like structure as a minimum-energy geometry. The distortion from planarity of the saddle-like cyclooctatetrathiophene structure is characterized by the folding angle  $\alpha$  that defines the tilting of the thiophene rings with respect to the central molecular plane. Figure S2 displays the most representative bond length values calculated for the core of both CoTh and **CoTh-TTPA**. Figure S3 displays the theoretical simulation of the absorption spectra calculated for **CoTh-TTPA** from the electronic transitions computed at the TDDFT B3LYP/6-31G\*\* level in CH<sub>2</sub>Cl<sub>2</sub> solution. Table S1 gathers the vertical excitation energies (*E*), the oscillator strengths (*f*) and the electronic descriptions in terms of oneelectron molecular orbital excitations calculated for the most relevant S<sub>0</sub>  $\rightarrow$  S<sub>n</sub> electronic transitions of **CoTh-TTPA** in CH<sub>2</sub>Cl<sub>2</sub>. Figure S4 depicts the topology and energy of the frontier molecular orbitals participating in the S<sub>0</sub>  $\rightarrow$  S<sub>n</sub> transitions quoted in Table S1.



**Figure S1.** B3LYP/6-31G\*\*-optimized geometries calculated in  $CH_2Cl_2$  solution for the CoTh core and the **CoTh-TTPA** HTM. The folding angle  $\alpha$  that characterizes the saddle-like structure of cyclooctatetrathiophene is quoted.



**Figure S2.** Optimized bond lengths (in Å) calculated at the B3LYP/6-31G\*\* level, in  $CH_2Cl_2$  solution, for the CoTh core and the **CoTh-TTPA** HTM. For the latter, the terminal TPA pendant groups have been partially omitted and only the bond lengths calculated for the core are shown.



**Figure S3**. Stick and convoluted absorption spectra computed for **CoTh-TTPA** at the TDDFT B3LYP/6-31G\*\* level in  $CH_2Cl_2$ . The TDDFT stick spectrum was convoluted with Gaussian functions of full-width at half maximum (FWHM) of 0.25 eV.

	- <b>F</b>
S1 2.38 / 521 0.410	$H \rightarrow L (96)$
S <sub>2</sub> 2.53 / 491 0.908	$H-1 \rightarrow L (97)$
S <sub>3</sub> 2.74 / 453 0.217	$H – 2 \rightarrow L (98)$
S <sub>5</sub> 2.87 / 431 0.872	$\mathrm{H} \rightarrow \mathrm{L}{+1} \ (95)$
S <sub>6</sub> 2.98 / 416 0.637	$\mathrm{H-1} \rightarrow \mathrm{L+1} \ (95)$
S <sub>7</sub> 3.19/389 0.473	$H – 2 \rightarrow L (81)$
	$\mathrm{H-1} \rightarrow \mathrm{L+1} \ (14)$
S <sub>11</sub> 3.33/373 0.225	$\text{H3} \rightarrow \text{L+-1} (16)$
	$\mathrm{H}\mathrm{1} \rightarrow \mathrm{L}\text{+}\mathrm{2}~(\mathrm{64})$
	$\mathrm{H} \rightarrow \mathrm{L+3}~(17)$
S <sub>13</sub> 3.51 / 353 0.404	$H-5 \rightarrow L (16)$
	$\text{H}2 \rightarrow \text{L+-}2 \ (69)$
S <sub>36</sub> 4.06 / 305 0.450	$\text{H3} \rightarrow \text{L+-11} (13)$
	$H – 2 \rightarrow L + 12 (13)$
	$\text{H-1} \rightarrow \text{L+10} \text{ (26)}$
	$\mathrm{H} \rightarrow \mathrm{L+9}~(19)$
	$\mathrm{H} \rightarrow \mathrm{L}{+}13~(21)$
S <sub>38</sub> 4.06 / 305 0.535	$\text{H3} \rightarrow \text{L+-13} (10)$
	$\text{H}2 \rightarrow \text{L+-10} (13)$
	$\text{H-1} \rightarrow \text{L+12} \text{ (24)}$
	$\mathrm{H} \rightarrow \mathrm{L}{+}11~(36)$

**Table S1.** Lowest-energy singlet excited states calculated at the TDDFT B3LYP/6-31G\*\* level for **CoTh-TTPA** in  $CH_2Cl_2$  solution. Vertical excitation energies (*E*), oscillator strengths (*f*) and dominant monoexcitations with contributions (within parentheses) greater than 10%.

<sup>a</sup> H and L denotes HOMO and LUMO, respectively.



**Figure S4.** Isovalue contours ( $\pm 0.03$  a.u.) and energies calculated at the B3LYP/6-31G\*\* level in CH<sub>2</sub>Cl<sub>2</sub> for selected molecular orbitals of **CoTh-TTPA**.

**Oxidized species**. B3LYP/6-31G\*\* calculations in  $CH_2Cl_2$  were used to investigate the molecular structure and charge distribution of the four-armed **CoTh-TTPA** HTM in different oxidation states, from the monocation to the tetracation. The radical cation species was computed as a doublet open-shell species. The dication was calculated both as a singlet closed-shell species, in which both electrons are extracted from the same orbital, and as a triplet open-shell species, in which the electrons are extracted from different orbitals. The triplet state was found to be more stable than the singlet state by 0.11 eV. In the case of the trication, doublet and quadruplet open-shell states were computed. The quadruplet state turned out to be the most stable by 0.21 eV. For the tetracation, the quintet state is found to be the most stable followed by the triplet (0.52 eV) and singlet (0.65 eV) states. Table S2 gathers the Mulliken atomic charges computed for the central CoTh core and the peripheral TPA groups of the different oxidized species of **CoTh-TTPA** in their most stable electronic state.

**Table S2.** Mulliken atomic charges (in e) computed for the central CoTh core and the TPA units of **CoTh-TTPA** in different oxidized states.



Molecular fragment	Neutral	Cation	Dication	Trication	Tetracation
CoTh	-0.508	-0.227	-0.116	-0.102	-0.067
TPA-1	0.127	0.307	0.529	0.775	1.017
TPA-2	0.127	0.307	0.529	0.775	1.017
TPA-3	0.127	0.307	0.529	0.776	1.017
TPA-4	0.127	0.307	0.529	0.776	1.017

Figure S5 represents the potential energy surfaces for the neutral and cation states of two molecules (labelled as 1 and 2) involved in an intermolecular charge transfer process. The intramolecular reorganization energy ( $\lambda$ ) consists of two terms related to the geometry relaxation energies of one molecule going from the fully relaxed ground state of the neutral species to the cation state (Figure S5, left) and a neighbouring molecule evolving in the opposite way (Figure S5, right),

$$\lambda = \lambda_1 + \lambda_2 \qquad \qquad \wedge * \text{ MERGEFORMAT (1)}$$
$$\lambda_1 = E \ (M1) - E \ (M1^+) \qquad \qquad \wedge * \text{ MERGEFORMAT (2)}$$
$$\lambda_2 = E \ (M2^+) - E \ (M2) \qquad \qquad \wedge * \text{ MERGEFORMAT (3)}$$

Here, E(M1) and  $E(M1^+)$  for molecule 1 are the energies of the positively charged molecule (the cation) at the equilibrium geometry of the neutral molecule and the relaxed cation, respectively, and  $E(M2^+)$  and E(M2) for molecule 2 are, accordingly, the energies of the neutral molecule at the equilibrium geometry of the cation and the neutral molecule, respectively.



**Figure S5.** Scheme of the potential energy surfaces of the neutral state (N) and the cation state (C) for two molecules (1 and 2) involved in a charge (hole) transfer process.  $\lambda_1$  and  $\lambda_2$  are the two contributions to the total intramolecular reorganization energy ( $\lambda$ ).

### 4. Device Preparation

Conductive FTO glass (NSG10) was sequentially cleaned by sonication in a 2 % Helmanex solution and isopropanol for 20 min respectively. A 20 to 50 nm titania blocking layer was applied on the substrates by spraying a solution of titanium diisopropoxide bis(acetylacetonate) in ethanol at 450 °C. For the mesoporous TiO<sub>2</sub> layer, 30 NR-D titania paste from Dyesol diluted in ethanol (ratio 1:8 by weight) was applied by spin-coating at 3000 rpm for 30 s followed by a sintering step at 500 °C for 30 min. After cooling down the substrates, a Li-treatment was applied by spincoating 80 µL of a solution of tris(bis(trifluoromethylsulfonyl)imide) (Li-TFSI) in acetonitrile (15 mg mL<sup>-1</sup>) onto the mesoporous layer, followed by a sintering step at 500 °C for 30 min to decompose the Li-salt as previously described. The [FAPbI<sub>3</sub>]<sub>0.85</sub>[MAPbBr<sub>3</sub>]<sub>0.15</sub> perovskite layers were fabricated by a single step spin-coating procedure. For the perovskite precursor solution 508 mg of PbI<sub>2</sub> (TCI), 68 mg PbI<sub>2</sub> (TCI), 180.5 mg formamidinium iodide (Dyesol) and 20.7 mg methylammonium bromide (Dyesol) were dissolved in a 1:4 mixture of DMSO:DMF. The perovskite solution was spun at 5000 rpm for 30 s using a ramp of 3000 rpm s<sup>-1</sup>. 17 s prior to the end of the spin-coating sequence, 100 µL of chlorobenzene were poured onto the spinning substrate. Afterwards the substrates were transferred onto a heating plate and annealed at 100 °C for 45 min. In the case of [(FAPbI<sub>3</sub>)<sub>0.87</sub>(MAPbBr<sub>3</sub>)<sub>0.13</sub>]<sub>0.92</sub>[CsPbI<sub>3</sub>]<sub>0.08</sub> based devices, the Litreatment was replaced by a SnO<sub>2</sub> layer applied by spin-coating at 3000 rpm for 30s. The perovskite was formed by the solution of 178.94 mg formamidinium iodide (Dyesol), 17.41 mg, methylammonium bromide (Dyesol), 57.06 mg PbBr<sub>2</sub> (TCI), 27.02 mg CsI and 548.60 mg PbI<sub>2</sub> (TCI) in a 1:3.5 mixture of DMSO:DMF. The substrates were annealed at 100 °C for 1h. The hole-transporting materials were applied from solutions in chlorobenzene (for spiro-OMeTAD and CoTh-TTPA). Optimized concentrations were found to be 20 mM for CoTh-TTPA and 70 mM for spiro-OMeTAD respectively. Tert-butylpyridine (Tbp), tris(2-(1H-pyrazol-1-yl)-4-tertbutylpyridine)cobalt(III) (FK209) and Li-TFSI were added as additives. Equimolar amounts of additives were added for all hole transporters: 330 mol% Tbp, 50 mol% Li-TFSI from a 1.8 M stock solution in acetonitrile and 6 mol% FK209 from a 0.25 M stock solution in acetonitrile. The final HTM solutions were spin-coated dynamically onto the perovskite layers at 3000 rpm for 30 s. The gold electrodes were deposited by thermal evaporation of 70 nm gold using a shadow mask under high vacuum conditions.

# 5. Solar Cell Characterization

The photovoltaic device performance was analyzed using a VeraSol LED solar simulator (Newport) producing 1 sun AM 1.5G (100 W cm<sup>-2</sup>) simulated sunlight. Current density-voltage (J-V) curves were measured in air with a potentiostat (Keithley). The light intensity was calibrated with an NREL certified KG5 filtered Si reference diode. The solar cells were masked with a metal aperture of 0.16 cm<sup>2</sup> to define the active area. The density current-voltage curves were recorded scanning at 10 mV s<sup>-1</sup>.

#### 5.1 Hysteresis curves



Figure S6. Hysteresis curve of the [FAPbI<sub>3</sub>]<sub>0.85</sub>[MAPbBr<sub>3</sub>]<sub>0.15</sub>/CoTh-TTPA cell.



Figure S7. Hysteresis curve of the [FAPbI<sub>3</sub>]<sub>0.85</sub>[MAPbBr<sub>3</sub>]<sub>0.15</sub>/spiro-OMeTAD reference cell.



**Figure S8.** Hysteresis curve of the [(FAPbI<sub>3</sub>)<sub>0.87</sub>(MAPbBr<sub>3</sub>)<sub>0.13</sub>]<sub>0.92</sub>[CsPbI<sub>3</sub>]<sub>0.08</sub>/spiro-OMeTAD reference cell.



Figure S9. Hysteresis curve of the [(FAPbI<sub>3</sub>)<sub>0.87</sub>(MAPbBr<sub>3</sub>)<sub>0.13</sub>]<sub>0.92</sub>[CsPbI<sub>3</sub>]<sub>0.08</sub>/CoTh-TTPA cell.

### 5.2 SEM images

Scanning electron microscope (SEM) images were taken by using a high-resolution scanning electron microscope ZEISS Merlin.



Figure S10. SEM images of the surface of the HTMs on top of the perovskites: a) spiro-OMeTAD/[FAPbI<sub>3</sub>]<sub>0.85</sub>[MAPbBr<sub>3</sub>]<sub>0.15</sub>; b) spiro-OMeTAD/[(FAPbI<sub>3</sub>)<sub>0.87</sub>(MAPbBr<sub>3</sub>)<sub>0.13</sub>]<sub>0.92</sub>[CsPbI<sub>3</sub>]<sub>0.08</sub>; c) CoTh-TTPA/[FAPbI<sub>3</sub>]<sub>0.85</sub>[MAPbBr<sub>3</sub>]<sub>0.15</sub>; d) CoTh-TTPA/[(FAPbI<sub>3</sub>)<sub>0.87</sub>(MAPbBr<sub>3</sub>)<sub>0.13</sub>]<sub>0.92</sub>[CsPbI<sub>3</sub>]<sub>0.08</sub>.

### **5.3 EQE Measurements**

External quantum efficiency (EQE) measurements were performed with an IQE-200B Quantum Efficiency Measurement system from Newport in the range of 350 to 820 nm using a step size of 10 nm.



Figure S11. EQE spectra using [(FAPbI<sub>3</sub>)<sub>0.87</sub>(MAPbBr<sub>3</sub>)<sub>0.13</sub>]<sub>0.92</sub>[CsPbI<sub>3</sub>]<sub>0.08</sub>/CoTh-TTPA.



Figure S12. EQE spectra using [(FAPbI<sub>3</sub>)<sub>0.87</sub>(MAPbBr<sub>3</sub>)<sub>0.13</sub>]<sub>0.92</sub>[CsPbI<sub>3</sub>]<sub>0.08</sub>/Spiro-OMeTAD.

# 5.4 Device statistics



**Figure S13.** Efficiency distribution of devices incorporating **CoTh-TTPA** fabricated with each perovskite.

# 6. Steady-State Photoluminescence

Photoluminescence spectra were recorded using a LS-55 photoluminescence spectrometer from PerkinElmer.



**Figure S14.** Steady state photoluminescence measured using an excitation wavelength of 580 nm. The samples were prepared from a stack of glass/perovskite/HTM and measured from the HTM side. Double cation perovskite (left) and triple cation Cs-perovskite (right) show similar trends in terms of quenching, although the latter is much more effective than the former, especially for **CoTh-TTPA**.

# 7. Lateral conductivity measurements

For the conductivity measurements, the different HTMs were spin-coated from their corresponding solutions in chlorobenzene onto substrates having interdigitated gold electrodes with a channel length of  $2.5\mu m$ . The same molar concentration as for the device preparation was used and 6% FK209 were added as dopant. Current-voltage curves were recorded in the range from -10 to 10 V and the corresponding conductivity values were calculated using Ohms law.

# 8. Supplementary figures



Figure S16. <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, 298 K) of CoTh-TTPA.



Figure S17. HR-MALDI-TOF mass spectrum of CoTh-TTPA.

# 9. References

<sup>4</sup> Gaussian16, Revision A.03, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, D. J. Fox, Gaussian Inc. Wallingford CT, **2016**.

<sup>5</sup> a) C. Lee, W. Yang, R. G. Parr, *Phys. Rev. B* **1988**, *37*, 785-789; b) A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 5648-5652.

<sup>6</sup> M. M. Francl, W. J. Pietro, W. J. Hehre, J. S. Binkley, M. S. Gordon, D. J. Defrees, J. A. Pople, *J. Chem. Phys.* **1982**, *77*, 3654-3665.

<sup>7</sup> a) J. Tomasi, M. Persico, Chem. Rev. **1994**, 94, 2027–2094; b) J. Tomasi, B. Mennucci, R. Cammi, *Chem. Rev.* **2005**, 105, 2999–3093; c) C. S. Cramer, D. G. Truhlar, in: Solvent Effects and Chemical Reactivity (Eds.: O. Tapia, J. Bertrán), Kluwer, Dordrecht, The Netherlands, **1996**, p. 1–80.

<sup>8</sup> a) M. E. Casida, C. Jamorski, K. C. Casida, D. R. Salahub, *J. Chem. Phys.* **1998**, 108, 4439-4449; b) C. Jamorski, M. E. Casida, D. R. Salahub, *J. Chem. Phys.* **1996**, 104, 5134-5147; c) M. Petersilka, U. J. Gossmann, E. K. U. Gross, *Phys. Rev. Lett.* **1996**, 76, 1212-1215.

<sup>9</sup> <u>http://www.chemcraftprog.com</u>

<sup>&</sup>lt;sup>1</sup> Mohammad Afsar Uddin, Youngkwon Kim, Robert Younts, Wonho Lee, Bhoj Gautam, Joonhyeong Choi, Cheng Wang, Kenan Gundogdu, Bumjoon J. Kim, and Han Young Woo, *Macromolecules* **2016**, *49*, 6374–6383.

<sup>&</sup>lt;sup>2</sup> Yong Wang, Dewen Gao, Jianwu Shi, Yuhe Kan, Jinsheng Song, Chunli Li, Hua Wang, *Tetrahedron* **2014**, *70*, 631-636.

<sup>&</sup>lt;sup>3</sup> Yangguang Wang, Zhihua Wang, Dongfeng Zhao, Zhen Wang, Yangxiang Cheng, Hua Wang, Synlett **2007**, *15*, 2390-2394