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Electronic Supplementary Information for:

An electron acceptor based on indacenodithiophene and 1,1-dicyanomethylene-3-indanone for fullerene-free organic solar cells

Huitao Bai,[ac] Yifan Wang,[ac] Pei Cheng,[ac] Jiayu Wang,[b] Yao Wu,[b] Jianhui Hou[a] and Xiaowei Zhan[b]*

[a] *Beijing National Laboratory for Molecular Sciences, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China.*

[b] *Department of Materials Science and Engineering, College of Engineering, Peking University, Beijing 100871, China. E-mail: xwzhan@pku.edu.cn*

[c] *University of Chinese Academy of Sciences, Beijing 100049, China.*

Materials. Unless stated otherwise, all the solvents and chemical reagents used were obtained commercially and were used without further purification. Toluene was distilled from sodium benzophenone under nitrogen before use. Compound **1** was synthesized according to a literature procedure.[1]

Synthesis of compound 2. To a three-necked round bottom flask were added compound **1** (986 mg, 0.8 mmol), 5-bromothiophene-2-carbaldehyde (382 mg, 2.0 mmol), and toluene (30 mL). The mixture was deoxygenated with argon gas for 15 min, and then $Pd(PPh_3)_4$ (70 mg, 0.06 mmol) was added. The mixture was refluxed for 24 h, and then allowed to cool to room temperature. A volume of 40 mL of KF solution (0.1 g mL^{-1}) was added, and the mixture was stirred at room temperature overnight to remove any tin impurities. Water (150 mL) was then added and the mixture extracted with $CHCl_3$ (2 × 150 mL). The organic phase was dried over anhydrous $MgSO_4$. After removing the solvent, the residue was purified using column chromatography on silica gel employing petroleum ether/CH_2Cl_2 (1:2) as an eluent, yielding a yellow-colored solid (808 mg, 90.0%). ^{1}H-NMR (400 MHz, CD_2Cl_2): δ 9.82 (s, 2H), 7.66 (d, J = 4 Hz, 2H), 7.50 (s, 2H), 7.30 (s, 2H), 7.27 (d, J = 4 Hz, 2H), 7.19 (d, J = 8 Hz, 8H), 7.11 (d, J = 8 Hz, 8H), δ 2.59 (m, 8H), 1.61 (m, 8H), 1.30 (m, 24H), 0.89 (m, 12H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 182.26, 157.22, 153.85, 147.86, 142.91, 141.92, 141.24, 141.17, 138.60, 137.31, 135.25, 128.55, 127.82, 123.61, 122.02, 117.77, 63.16, 35.59, 31.73, 31.35, 29.16, 22.61, 14.12. MS (MALDI-TOF): *m/z* 1128 (M^+). Anal. Calc. for $C_{74}H_{78}O_2S_4$: C, 78.82; H, 6.97. Found: C, 79.24; H, 7.12%.

Synthesis of DC-IDT2T. Compound **2** (200 mg, 0.177 mmol) and 1,1-dicyanomethylene-3-indanone (103 mg, 0.53 mmol) were dissolved in dry $CHCl_3$ (30 mL). The mixture was deoxygenated with argon gas for 15 min. Three drops of pyridine were then added and the mixture refluxed and stirred for 2 h under argon gas. After being allowed to cool to room temperature, water (100 mL) was added and the mixture was extracted with $CHCl_3$ (2 × 100 mL). The organic phase was dried over anhydrous $MgSO_4$. After removing the solvent, the residue was purified using column chromatography on silica gel employing petroleum ether/CH_2Cl_2 (1:2) as an eluent, yielding a black-colored solid (230 mg, 87.8%). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.82 (s, 2H), 8.68 (d, J = 8 Hz, 2H), 7.91 (d, J = 8 Hz, 2H), 7.73 (m, 6H), 7.49 (d, J = 4 Hz, 4H), 7.30 (d, J = 4 Hz, 2H), 7.19 (d, J = 8 Hz, 8H), 7.12 (d, J = 8 Hz, 8H), 2.60 (m, 8H), 1.64 (m, 8H), 1.30 (m, 24H), 0.88 (m, 12H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 188.49, 160.18, 158.17, 154.35, 154.22, 146.42, 144.82, 142.01, 140.89, 139.98, 139.08, 137.37, 136.75, 135.64, 135.56, 135.11, 134.40, 128.61, 127.79, 125.23, 124.42, 123.66, 123.24, 121.81, 118.01, 114.60, 114.52, 69.27, 63.12, 35.56, 31.70, 31.33, 29.09, 22.57, 14.08. MS (MALDI-TOF): *m/z* 1480 (M^+). Anal. Calc. for $C_{98}H_{86}N_4O_2S_4$: C, 79.53; H, 5.86; N, 3.79. Found: C, 79.23; H, 5.81; N, 3.74%. $\lambda_{s,\ max}$ = 700 nm (1.4×10^5 M^{-1} cm^{-1}).

Characterization. The ^{1}H and ^{13}C NMR spectra were measured using a Bruker AVANCE 400 MHz spectrometer employing tetramethylsilane (TMS; $\delta = 0$ ppm) as an internal standard. Elemental analysis was carried out using a FlashEA 1112 elemental analyzer. Mass spectra were measured using a Bruker Daltonics Biflex III MALDI-TOF Analyzer in the MALDI mode. Solution (chloroform) and thin film (on a quartz substrate) UV-vis absorption spectra were recorded using a Jasco V-570 spectrophotometer. Electrochemical measurements were carried out under nitrogen in a deoxygenated solution of tetra-*n*-butylammonium hexafluorophosphate (0.1 M) in acetonitrile using a potential scan rate of 100 mV s^{-1} employing a computer-controlled Zahner IM6e electrochemical workstation, a glassy-carbon working electrode coated with the DC-IDT2T film, a platinum-wire auxiliary electrode, and an Ag/AgCl electrode as a reference electrode. The potentials were referenced to a ferrocenium/ferrocene ($FeCp_2^{+/0}$) couple using ferrocene as an external standard. Thermogravimetric analysis (TGA) measurements were performed using a Shimadzu thermogravimetric analyzer (Model DTG-60) under flowing nitrogen gas at a heating rate of 10 °C min^{-1}. Differential scanning calorimetry (DSC) measurements were performed using a Mettler differential scanning calorimeter (DSC822e) under nitrogen gas at a heating rate of 10 °C min^{-1}. X-ray diffraction (XRD) of the thin films was performed in the reflection mode at 40 kV and 200 mA using Cu-Kα radiation in a 2 kW Rigaku D/max-2500 X-ray diffractometer. The nanoscale morphology of the blended films was observed using a Veeco Nanoscope V atomic force microscope (AFM) in the tapping mode.

Fabrication and characterization of the photovoltaic cells. Organic solar cells were fabricated with the structure, ITO/PEDOT: PSS/donor: acceptor/Ca/Al. Patterned indium tin oxide (ITO) glass (sheet resistance = 15 $\Omega\ \square^{-1}$) was precleaned in an ultrasonic bath with acetone and isopropanol, and treated in an ultraviolet–ozone chamber (Jelight Company, USA) for 23 min. A thin layer (35 nm) of poly(3,4-ethylenedioxythiophene): poly(styrene sulfonate) (PEDOT: PSS, Baytron PVP AI 4083, Germany) was spin-coated onto the ITO glass, and then baked at 150 °C for 20 min. A donor: acceptor mix (20 mg mL^{-1} in total) in *o*-dichlorobenzene with 15% chloroform was spin-coated on the PEDOT: PSS layer to form a photosensitive layer (ca. 70 nm thick). The calcium layer (ca. 20 nm) and the aluminum layer (ca. 100 nm) were then evaporated onto the surface of the photosensitive layer under vacuum (ca. 10^{-5} Pa) to form the negative electrode. The active area of the device was 4 mm^2. The *J–V* curve was measured using a computer-controlled B2912A Precision Source/Measure Unit (Agilent Technologies). An XES-70S1 (SAN-EI Electric Co., Ltd.) solar simulator (AAA grade, 70 × 70 mm^2 photobeam size) coupled with AM 1.5 G solar spectrum filters was used as the light source, and the optical power at the sample was 100 mW cm^{-2}. A 2 × 2 cm^2 monocrystalline silicon reference cell (SRC-1000-TC-QZ) was purchased from VLSI Standards Inc. The incident photon to converted current efficiency (IPCE) spectrum was measured using a Solar Cell Spectral Response Measurement System QE-R3011 (Enlitech Co., Ltd.). The light intensity at each wavelength was calibrated using a standard single crystal Si photovoltaic cell.

Mobility measurements. Hole-only or electron-only diodes were fabricated using the architectures ITO/PEDOT: PSS/active layer/Au for holes and Al/active layer/Al for electrons. The mobility was extracted by fitting the current density–voltage curves using the Mott–Gurney relationship (space charge limited current).[2]

Computation details. Density functional theory calculations were performed with the Gaussian 09 program,[3] using the B3LYP functional.[4,5] All-electron double-ξ valence basis sets with polarization functions 6-31G* were used for all atoms.[6] Geometry optimizations were performed with full relaxation of all atoms in gas phase without solvent effects. Vibration frequency calculation was performed to check that the stable structures had no imaginary frequency. Charge distribution of the molecules was calculated by Mulliken population analysis.

Table S1 OSC performance at different PBDTTT-C-T: DC-IDT2T weight ratio

PBDTTT-C-T: DC-IDT2T	V_{OC} (V)	J_{SC} (mA cm^{-2})	FF (%)	PCE (%) best	PCE (%) average
2:1	0.89	7.06	49.1	3.09	2.87
1.5:1	0.90	7.95	50.1	3.56	3.29
1.2:1	0.90	8.33	52.3	3.93	3.72
1:1	0.90	8.02	50.5	3.64	3.49
1:1.5	0.90	7.35	49.5	3.27	3.10

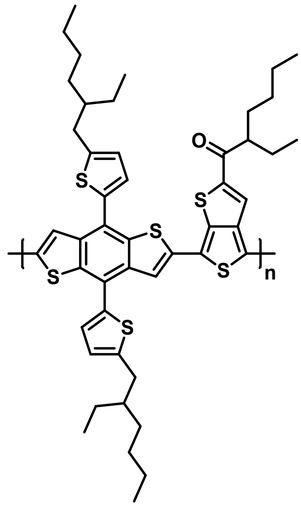


Fig. S1 Chemical structure of PBDTTT-C-T.

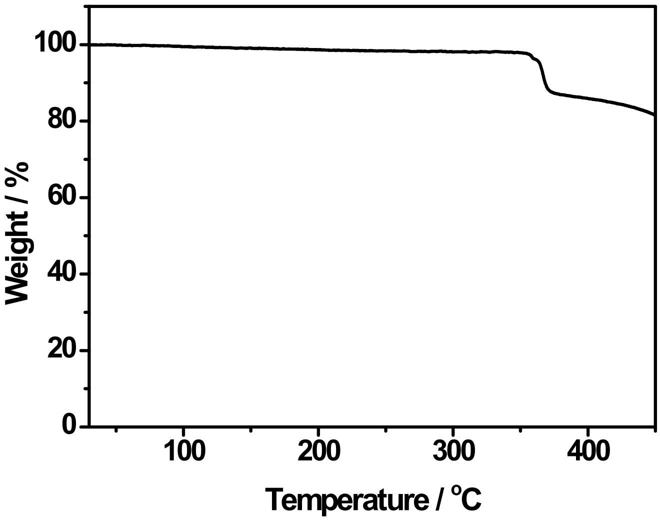


Fig. S2 TGA curve of DC-IDT2T.

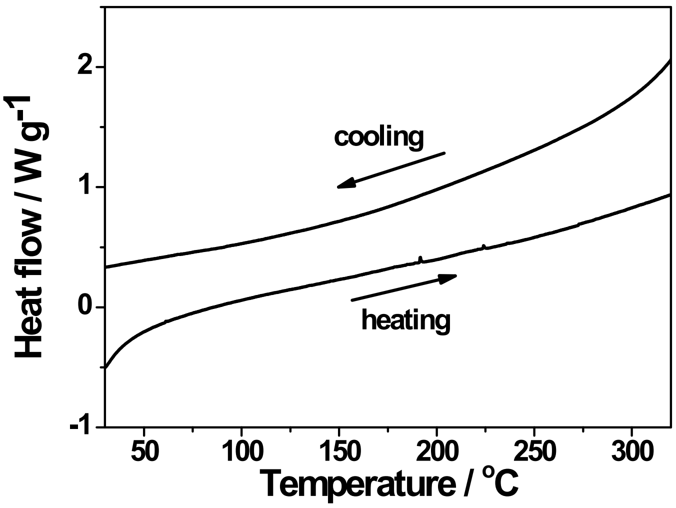


Fig. S3 DSC curves of DC-IDT2T.

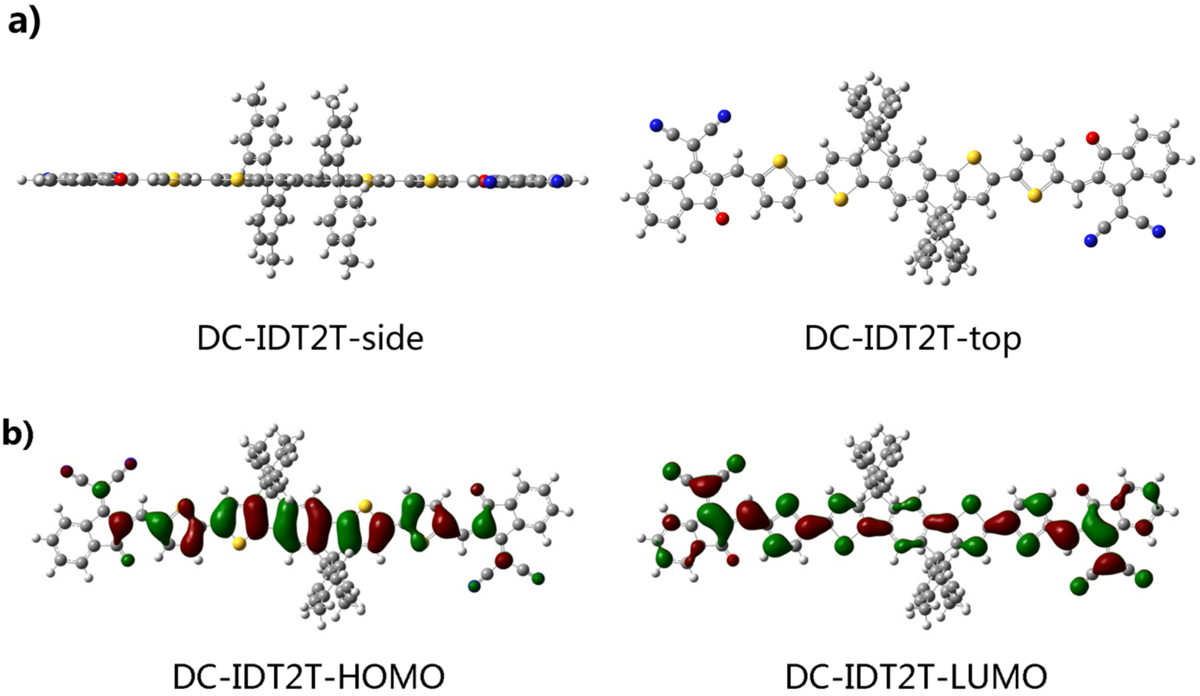


Fig. S4 a) Optimized geometries and b) molecular orbitals of DC-IDT2T. The alkyl chains are replaced with methyl groups for computational simplicity.

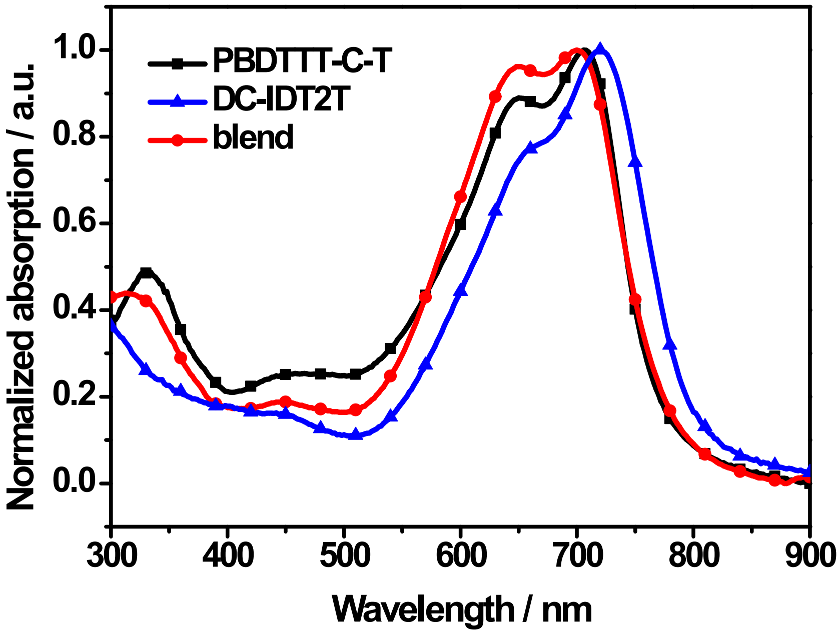
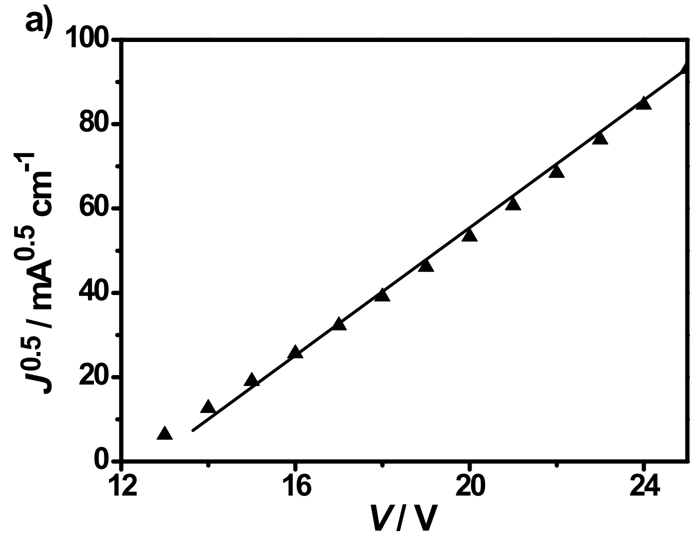
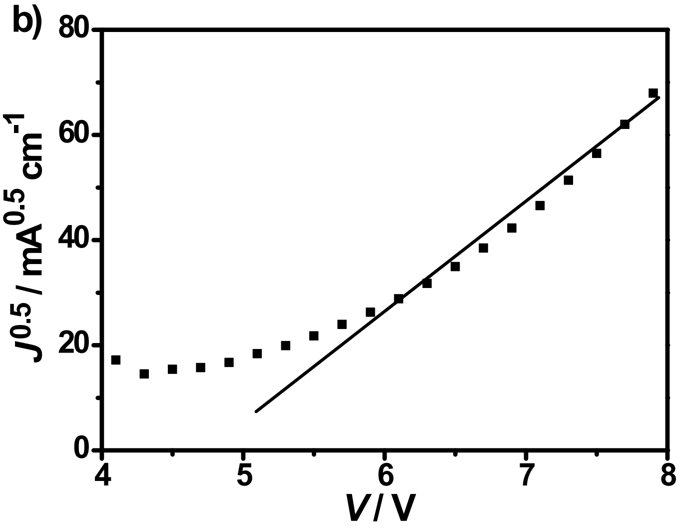


Fig. S5 Absorption spectra of thin films based on PBDTTT-C-T, DC-IDT2T and PBDTTT-C-T: DC-IDT2T (1.2:1, w/w) blend.





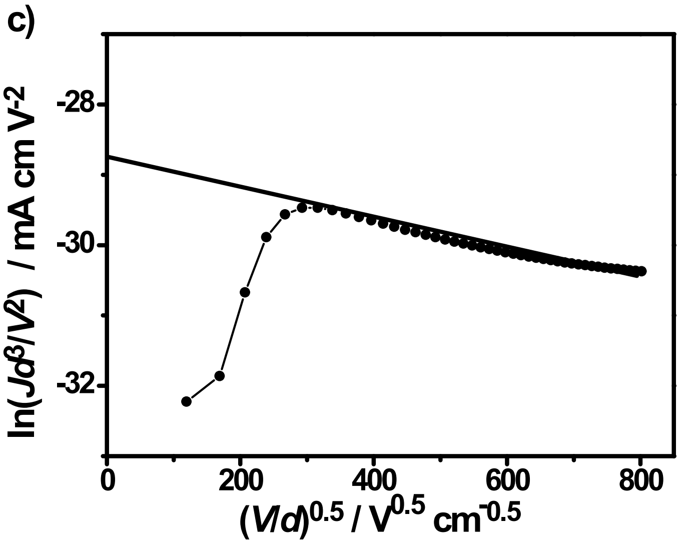


Fig. S6 J-V curves for a) electron-only devices based on DC-IDT2T neat film; b) electron-only devices based on PBDTTT-C-T: DC-IDT2T blend film; c) hole-only devices based on PBDTTT-C-T: DC-IDT2T blend film.

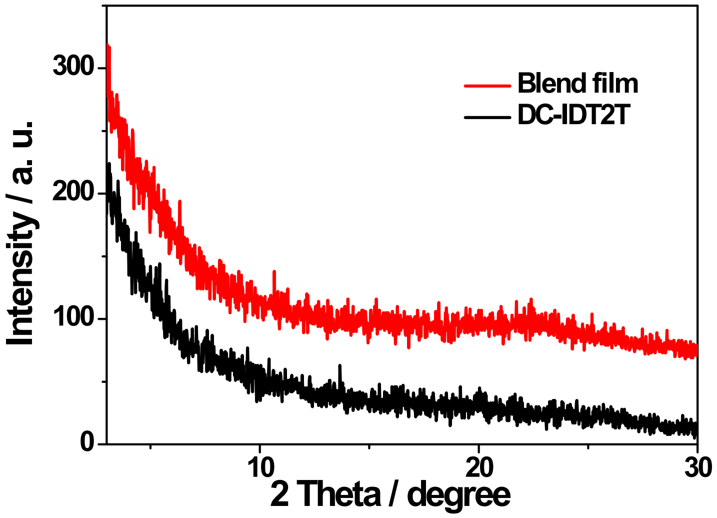


Fig. S7 XRD patterns of films of DC-IDT2T and PBDTTT-C-T: DC-IDT2T blend.

References

1 Y. C. Chen, C. Y. Yu, Y. L. Fan, L. I. Hung, C. P. Chen and C. Ting, *Chem. Commun.*, 2010, **46**, 6503.

2 G. G. Malliaras, J. R. Salem, P. J. Brock and C. Scott, *Phys. Rev. B*, 1998, **58**, R13411.

3. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G.

Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian 09, Revision A.01, Gaussian, Inc., Wallingford CT, 2009.

4. C. T. Lee, W. T. Yang and R. G. Parr, *Phys. Rev. B*, 1988, **37**, 785.

5. A. D. Becke, *J. Chem. Phys.*, 1993, **98**, 5648.

6. R. Krishnan, J. S. Binkley, R. Seeger and J. A. Pople, *J. Chem. Phys*., 1980, **72**, 650.