Supporting Information

For

Efficient and thermally stable non-doped red OLEDs based on a "bird-like" donor-acceptor fluorophore with aggregation induced emission enhancement and intramolecular charge transfer

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Experimental Details:

Materials:

All the solvents for UV and FL analyses were used as spectroscopic grade. Column chromatography was performed on silica gel (100-200 mesh). Thin-layer chromatography (TLC) was performed on precoated silica gel F-254 plates (0.25 mm, E. Merck). Phenothiazine, 2-Ethylhexylbromide, Methyl 6-bromo-2-naphthoate, Sodium cyanide, DIBAL-H (1 M in heptanes), 9,9-dihexylfluorene and tetrakis-ztriphenylphosphine) palladium(0) were purchased from Sigma Aldrich and used as received for the synthesis of monomer and copolymers.

Instrumentation:

¹H and ¹³C NMR spectra were recorded on a 400 MHz Bruker spectrophotometer using CDCl₃ with tetramethylsilane (TMS, d = 0) as the internal standard. Mass spectra were recorded on a MALDI-mass Bruker ultraflextreme spectrometer by using a 4-HCCA (a-cyano-4-hydroxycinnamic acid) matrix. Elemental analysis was carried out using a Euro Vector S.P.A, Euro EA 3000 CHNS elemental analyzer.

Fourier transform infrared (FT-IR) spectra of the compounds were recorded on an ABB BOMEM MB3000 spectrometer using KBr pellets. UV-visible absorbance spectra were recorded on a Varian Carey 50 Bio UV-visible spectrophotometer. Fluorescence spectra of the monomer and copolymers were recorded on a Varian Carey Eclipse fluorescence spectrophotometer. Cyclic voltammetry measurements were done using CHI 600D electrochemical work stations using Ag/AgCl, platinum disc and platinum wire as reference, working and counter-electrodes respectively. Cyclic voltammetry was performed by coating a thin layer of PTNAA luminogen on a platinum disc electrode and measurements were performed in acetonitrile medium with tetrabutylammonium hexafluorophosphate (0.1 M [Bu₄N] PF₆) as a supporting electrolyte. Dynamic light scattering (DLS) experiments were performed on a Malvern, DLS instrument. Fluorescence lifetime experiments were conducted on EDINBURGH (UK) and FLS 980 TCSPC instruments. Atomic force micrographs (AFM) were obtained on a RUSSIA model: NTEGRA PRIMA instrument under ambient conditions using NT-MDT solver software for analysis, Ireland. The high resolution scanning electron microscopy (HRSEM) analysis were performed using HITACHI S-4800. Samples for AFM and SEM were prepared by spin coating 300 microliters of the chloroform solution (2 mg mL⁻¹) and over the surface area of 1.8 cm² of an ITO coated glass substrate to simulate the end use device conditions. The absolute quantum yield of PTNAA was collected by measuring the total light output in all directions in an integrating sphere using EDINBURGH (UK) and FLS 980 TCSPC instruments. GIXRD studies were performed on films of the PTNAA coated on ITO substrates using a Bruker AX D8 advance X-ray diffractometer with a Cu Ka wavelength of 1.5406 Å. Density functional theory (DFT) calculations were performed using the B3LYP functional. The basis set used for the C, H, and N atoms was 6-31 Gs.

OLEDs fabrication and measurement: OLEDs of PNAA were fabricated using indium tin oxide (ITO) with a sheet resistance of 10 O square⁻¹. The substrates were cleaned by a series of ultrasonic processing with acetone, detergent, and deionized water in an ultrasonic solvent bath. After cleaning in the solvent bath they were then baked in a heating chamber at 120 °C and treated with oxygen plasma for 25 min before use. The PEDOT-PSS (10–40 nm) solution was spin-coated on cleaned ITO substrates and baked

in a heating chamber at 200 °C for one hour. After the above process 300 mL of PTNAA in CHCl₃ (solution with 1 mg/mL concentration) were spin-coated at 2000 rpm for 60 seconds to get uniform film (with thickness 100–150 nm) and the aluminium was coated at 105 Torr. Current–voltage (I–V) characteristics were studied using a Keithley 2400 sourcemeter. Luminescence–voltage (L–V) characteristics of the OLEDs were performed using a NUCLEONIX type 168 PMT housing with drawer assembly. Electroluminescence spectra of the OLEDs were further measured using a Carey Eclipse fluorescence spectrophotometer. Commission Internationale de l'Eclairage (CIE) color coordinate values of the thin films of the LEDs were standardized using a Konica Minolta CS-100 Chromameter in automated mode.

Synthesis procedure of PTNAA monomer:



(D2-A1-D1-A1-D2)-PTNAA

Scheme 1 Synthetic route to AIE monomer of PTNAA (i) DIBAL-H in THF, 0 to 25 °C, for 12 hr; (ii) SOCl₂, ZnCl₂, DME, 0 °C for 2 hrs and then RT for 12 hrs; (iii) NaCN, aq CH₃CN, reflux for 12 hrs

(iv) Ethylhexyl-bromide, DMF, NaH stirred for 12 hrs at RT; (v) 1,2-dichloroethane, POCl₃, DMF reflex for 12 hrs; (vi) KOt-Bu/methanol, for 24 hrs at RT.

(6-bromonaphthalen-2-yl) methanol: (NA-OH)

To a completely-dried 250 mL, round bottom flask was added methyl 6-bromo-2-naphthoate (10 g, 3.8 x 10^{-2} mol) and anhydrous THF (50 mL) under a nitrogen atmosphere. The solution was cooled to 0 °C and slowly charged into a solution of DIBAL-H (1 M in heptane, 13.5 mL (11.38 g), 8.0 x 10^{-2} mol) was added dropwise to the reaction mixture. The reaction mixture was heated up to room temperature and agitated overnight. The reaction mixture was quenched slowly by pouring into a HCl (4N aq. 30 mL) at 0 °C. The reaction mixture was stirred for 45 min and the organic layer was separated using separating funnel. The organic layer was washed with HCl (4N aq. 20 mL), NaHCO₃ (5% aq. 75 mL), and washed with brine solution (50 mL). The organic layer was concentrated over MgSO4, filtrated by Celite and concentrated to dryness. EtOAc (10 mL) and hexanes (80 mL) were added to the resultant product. Filtration by filter paper and drying under vacuum gave (NA-OH) as a white solid (~ 8.45 g, 3.58 x 10^{-2} mol, yield = 94%). Spectral data for (NA-OH):

¹H NMR (400 MHz, CDCl₃) δ 7.91 (s, 1H), 7.71 – 7.58 (m, 3H), 7.44 (dd, *J* = 22.3, 8.6, 1.7 Hz, 2H), 4.76 (s, 2H), 1.72 (s, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 137.84, 132.96, 130.78, 128.76, 128.56, 128.51, 126.39, 125.14, 124.26, 118.81, 64.22. Elemental analysis: Calculated (%) for C₁₁H₉BrO: C, 55.72; H, 3.83, Br, 33.70; Found: C, 54.97; H, 3.78; Br, 33.69.



Figure S1 ¹H and ¹³C NMR spectrum of NA-OH

2-bromo-6-(chloromethyl) naphthalene: (NA-Cl)

To a 250 mL round bottom flask was added (6- bromonaphthalen-2-yl) methanol (NA-OH) (5, 2.12 x 10^{-2} mol), ZnCl₂ (115 mg, 0.085 x 10^{-2} mol) and DME (70 mL). The reaction mixture was cooled to 0 °C and SOCl₂ (3.1 mL (5g), 4.24 x 10^{-2} mol) was slowly added. The resulting mixture was stirred at 0 °C for 2 hours, and then at room temperature overnight. The solvent was removed by rotary evaporation. Hexanes (100 mL) were added to the crude product. Filtration by filter paper and drying under vacuum gave **NA-Cl** as a white solid (5.14 g, 2.0 x 10^{-2} mol, yield = 95%). Spectral data for **NA-Cl**:

¹H NMR (400 MHz, CDCl₃) δ 7.92 (s, 1H), 7.74 – 7.60 (m, 3H), 7.48 (m, *J* = 16.3, 8.6, 1.7 Hz, 2H), 4.66 (s, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 134.33, 133.11, 130.57, 128.88, 128.80, 128.57, 126.77, 126.41, 126.30, 119.52, 45.26. Elemental analysis: Calculated (%) for C₁₁H₈BrCl: C, 51.70; H, 3.16, Br, 31.27; Found: C, 51.43; H, 3.21; Br, 31.19.



Figure S2 ¹H and ¹³C NMR spectrum of NA-Cl.

2-(6-bromonaphthalen-2-yl)acetonitrile (NA-CN) (1):

To a 250 mL round bottom flask was added 2- bromo-6-(chloromethyl)naphthalene (NA-Cl) (5 g, 1.95 x 10^{-2} mol) and NaCN (1.15 g, 2.34 x 10^{-2} mol), CH₃CN (75 mL) and H₂O (15 mL) The mixture was refluxed overnight under nitrogen. After cooling to room temperature, finally H₂O (70 mL) was added to the flask. The resulting organic layer was separated and the solvent was removed by rotary evaporation. Then H₂O (100 mL) and Methylene chloride (500 mL) was added to the mixture. The organic layer was separated, dried over MgSO₄, filtered through Celite and concentrated to dryness. The crude product was washed with CH₂Cl₂/hexanes (1:20 v/v). The organic compound was filtered by using filter paper and drying under vacuum gave NA-CN as a light yellow solid (4.54 g, 1.853 x 10^{-2} mol, yield = 95%). Spectral data for NA-CN:

¹H NMR (400 MHz, CDCl₃) δ 8.00 (d, *J* = 1.2 Hz, 1H), 7.81 – 7.67 (m, 3H), 7.59 (dd, *J* = 8.7, 1.9 Hz, 1H), 7.40 (dd, *J* = 8.5, 1.6 Hz, 1H), 3.90 (s, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 133.77, 131.77, 130.26, 129.85, 129.36, 128.16, 127.80, 126.85, 126.55, 120.58, 117.53, 23.83. Elemental analysis: Calculated (%) for C₁₂H₈BrN: C, 58.56; H, 3.28, Br, 32.47; Found: C, 58.49; H, 3.31; Br, 32.36. These spectral data match those previously reported for this compound.^{1,2}





Figure S3 ¹H and ¹³C NMR spectrum of NA-CN

(2-ethylhexyl)-10H-phenothiazine (PT-Al)

A 100 mL 3-neck flask was added with phenothiazine (5 g, 2.51×10^{-2} mol), NaH (0.8 g, 3.26×10^{-2} mol), and 50 mL of DMF. The resulting mixture was stirred for 30 min. Further, 2-Ethylhexylbromide (6.29 g, 3.26×10^{-2} mol) was added and the reaction mixture was stirred overnight at room temperature. The reaction mixture was quenched by water and extracted three times with chloroform. The combined organic fractions were washed with brine and dried over MgSO4. The solvent was removed under reduced pressure and the residue was purified by column chromatography using silica gel and *n*-hexane/ethylacetate (9/1; v/v) as the eluent to give PT-Al as a yellow viscous liquid (6.7 g, 2.15 x 10^{-2} mol, yield = 86%). Spectral data for PT-Al:

¹H NMR (400 MHz, CDCl₃) δ 7.14 – 6.99 (m, 4H), 6.87 – 6.76 (m, 4H), 3.67 (d, *J* = 7.0 Hz, 2H), 1.91 (dt, *J* = 12.3, 6.1 Hz, 1H), 1.35 (m, *J* = 30.2, 23.4, 7.4, 1.5 Hz, 8H), 0.83 (t, *J* = 7.5 Hz, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 145.96, 127.71, 127.22, 126.05, 122.49, 116.03, 51.17, 35.97, 30.93, 28.78, 24.25, 23.26, 14.24, 10.71. Elemental analysis: Calculated (%) for C₂₀H₂₅NS: C, 77.12; H, 8.09, N, 4.50, S, 10.29; Found: C, 76.98; H, 8.14, N, 4.39, S, 9.67.





Figure S4 ¹H and ¹³C NMR spectrum of PT-A1

10-(2-ethylhexyl)-10H-phenothiazine- 3,7-dicarbaldehyde (PT-(CHO)₂(2))

A 100 mL 2-neck flask was added with a solution of 10-(2- ethylhexyl)-10-phenothiazine (5.00 g, 1.60 x 10^{-2} mol) and dry DMF (5.87 g, 0.080 mol) in 1,2-dichloroethane (DCE) (50 mL), phosphorus oxychloride (11.9 mL (19.62 g), 12.8 x 10^{-2} mol) was added slowly at 0 °C. Then the reaction mixture was heated to reflux and maintained for overnight. The reaction mixture was quenched with addition of water and extracted three times with chloroform. The combined organic fractions were washed with brine solution and dried over MgSO₄. The solvent was removed under reduced pressure and the residue was purified by column chromatography using silica gel and ethylacetate/hexane (1/9; v/v) as the eluent to give the two different products, 10-(2-ethylhexyl)-phenothiazine-3-carbaldehyde and 10-(2-ethylhexyl)-10H- phenothiazine-3,7-dicarbaldehyde (3.17 g, 0.93 x 10^{-2} mol, yield = 54% of PT(CHO)₂. Spectral data for PT(CHO)₂:

¹H NMR (400 MHz, CDCl₃) δ 9.76 (s, 2H), 7.62 (dd, J = 8.4, 1.9 Hz, 2H), 7.56 (d, J = 1.8 Hz, 2H), 6.92 (d, J = 8.4 Hz, 2H), 3.78 (dd, J = 7.2, 1.1 Hz, 2H), 1.85 (dt, J = 12.5, 6.4 Hz, 1H), 1.41 – 1.27 (m, 4H), 1.22 – 1.13 (m, 4H), 0.79 (dt, J = 10.7, 7.3 Hz, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 189.93, 149.77, 132.15, 129.94, 128.89, 125.75, 116.38, 51.94, 36.15, 30.49, 28.43, 23.86, 22.95, 13.93, 10.41. Elemental analysis: Calculated (%) for C₂₂H₂₅NO₂S: C, 71.90; H, 6.86, N, 3.81, S, 8.73; Found: C, 71.87; H, 5.79, N, 3.63, S, 8.56.





Figure S5 ¹H and ¹³C NMR spectrum of PT(CHO)₂

(2Z,2'Z)-3,3'-(10-(2-ethylhexyl)-10H-phenothiazine-3,7-diyl)bis(2-(6-bromonaphthalene-2-yl)acrylonitrile) (PTNAA)

A mixture of compound PT-(CHO)₂ (2.00 g, 0.54×10^{-2} mol), NaCN (3.34 g, 1.36×10^{-2} mol) and methanol were placed in a 100-mL two-neck round bottom flask at room temperature. A catalytic amount of potassium tert-butoxide in methanol was added slowly into this reaction mixture. After 24 h, the product was filtered and dried. The crude solid was further purified by column chromatography on silica gel eluted with dichloromethane/hexane 3:2 afforded PTNAA as a red solid (4.04 g, 0.49 mol, yield = 91%). Spectral data for PTNAA:

¹H NMR (400 MHz, CDCl₃) δ 8.00 (d, *J* = 7.2 Hz, 2H), 7.93 (d, *J* = 5.2 Hz, 2H), 7.87 – 7.75 (m, 2H), 7.73 – 7.59 (m, 6H), 7.57 – 7.47 (m, 3H), 7.44 – 7.33 (m, 2H), 7.19 (s, 1H), 6.87 (m, *J* = 17.7, 10.5, 5.2 Hz, 2H), 6.58 (d, *J* = 8.6 Hz, 1H), 3.79 – 3.60 (m, 2H), 1.95 – 1.74 (m, 1H), 1.42 – 1.17 (m, 8H), 0.84 – 0.74 (m, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 146.74, 143.02, 140.84, 134.21, 132.34, 131.77, 130.43, 129.99, 129.81, 128.98, 128.74, 127.96, 127.04, 125.80, 123.54, 121.01, 118.20, 116.29, 108.94, 51.31, 36.22, 30.60, 28.53, 23.93, 23.05, 13.97, 10.48. MALDI mass m/z: Calculated for C₄₆H₃₇Br₂N₃S; 823.68; found, 823.16. Elemental analysis: Calculated (%) for C₄₆H₃₇Br₂N₃S: C, 67.08; H, 4.53, Br, 19.40, N, 5.10, S, 3.89; Found: C, 66.74; H, 4.57, Br, 19.31, N, 4.96, S, 3.73.





Figure S6 ¹H and ¹³C NMR spectrum of PTNAA.



Figure S7 HPLC of PTNAA monomer.



Figure S8 Maldi-TOF mass spectrometrum of PTNAA monomer.



Figure S9 Absorption spectrum of PTNAA monomer in varying polarity of the solvents.

Lippert- mataga study:

Solvatochromism is a characteristic behavior of dipolar molecules. In general, different polarity of solvent provides a usefull frame work for study of solvent dependent spectral shift. Using Lippertmataga study the influence of different polarity of solvents environment on photophysical property of organic luminogen can be understood. Lippert- mataga study reveals that the interactions between the solvent and dipolmoment of solute, the equation can be given as follows.

$$hc(v_{a} - v_{f}) = hc(v_{a}^{0} - v_{f}^{0}) - \frac{2(\mu_{e} - \mu_{g})}{a^{3}} \left[\frac{\varepsilon - 1}{2\varepsilon + 1} - \frac{n^{2} - 1}{2n^{2} + 1} \right]$$
$$a = (3M / 4N\pi d)^{1/3}; \left[\frac{\varepsilon - 1}{2\varepsilon + 1} - \frac{n^{2} - 1}{2n^{2} + 1} \right] = f(\varepsilon, n)$$
$$\mu_{g} = (m_{2} - m_{1}/2) [hca^{3}/2m_{1})^{1/2}$$
$$\mu_{e} = (m_{1} + m_{2}/2) [hca^{3}/2m_{1})^{1/2}$$

Where *h* is the Planck's constant (6.625x10⁻⁷ ergs), *c* is the velocity of light (2.997x10¹⁰ cm/s), "a' is the Radius of the cavity in which the fluorophore resides, derived from the Avogadro number (N), molecular weight(M), and density (d=1.0 g/cm³); v_a and v_f is wavenumber (cm⁻¹) of the absorption and

emission respectively; v_a^0 and v_f^0 are corresponds to the stokes shift when *f* is Zero; μ_e is the excited state dipole moment, μ_g is the ground state dipole moment; *f* is the orientation polarizability of the solvent; ε and n are the solvent dielectric and the solvent refractive intex, respectively. The detailed data are listed in Table S1.

				PTNAA			
Solvents	3	n	<i>f</i> (ε,n)	$\lambda_a(nm)$	$\lambda_f(nm)$	Stroke shift $(\lambda_a - \lambda_f) (cm^{-1})$	
Hevane	10	1 375	0.0012	116	548	1136	
Toluene	2.38	1.49	0.0012	440 441	559	4786	
Diethyl ether	4.34	1.35	0.167	439	567	5143	
Ethylacetate	6.02	1.372	0.200	437	573	5431	
Tetrahydrofurane	7.58	1.40	0.210	438	577	5500	
Methylene chloride	8.93	1.42	0.217	433	581	5883	
N'N-Dimethyl formamide	37	1.427	0.276	435	585	5784	
Acetone	20.7	1.35	0.284	443	588	5825	
Acetonitrile	37.5	1.34	0.305	434	593	6178	

Table S1. Detailed study of absorption and emission peak position of **PTNAA** in different polar solvents.

Where, ε and n are the solvent dielectric and the solvent refractive index, respectively; f is the orientational polarizability of the solvent; λ_a and λ_f absorption maximum and emission maximum respectively.

Table S2. Spectral properties of PTNAA monomer

Coumpound	$^{a}\lambda_{max}$ (Abs) (nm)		$^{c}\lambda_{max}$ (Emi) (nm) ^{d}F		uorescence lifetime	et SOL	fa TF
	Solution $b(\varepsilon)$	Thin film (Exc)	Solution	Thin film (Exc)	Thin film (T_1/T_2)	Ψρ	ΨŀΓ
PTNAA	328, 442	343, 483	573 (442)	605 (483)	6.47/2.06	57.7	71.9

 ${}^{a}\lambda_{max}$ (Abs), absorption maxima for solutions and thin films in nm; ${}^{b}(\varepsilon)$, extinction coefficient in dL g⁻¹ cm⁻¹. ${}^{c}\lambda_{max}$ (Emi), emission maxima for solutions and thin films in nm. T₁/T₂, life time of different decay channels from fluorescence lifetime experiment in ns for thin films; ${}^{e}\Phi_{PL}{}^{SOL}$ and ${}^{e\Phi}_{PL}{}^{TF}$, solution and thin film absolute PL quantum yields (in %) were measured using an integrating sphere.



Figure S10. (a) AFM micrograph of spun thin films from chloroform solution of PTNAA (inset GIXRD traces), (b) HRSEM micrograph ((scale bar for image is 2 μm).



Figure S11. Absorptin spectrum of PTNAA in varying percentage addition of water fraction in THFaggregated states.



Figure S12. DLS traces of PTNAA monomer with varying percentage compositions of water /THF

mixtures



Figure S13. (a) TGA curve: (b) DSC curve of PTNAA (Scan rate = 10° C min⁻¹ under the nitrogen).



Figure S14 Cyclic voltammetry traces of PTNAA



Table S3. Device characteristics of PTNAA copolymers.

Compound	HOMO ª (eV)	LUMO ^b (eV)	E ^{ele} /E ^{opt} /E ^{theo} ^c (eV)	^d η _c ^{max} (cd/A)	^e η _p ^{max} (Lm/W)	^f L ^{max} (cd/ m ²)	Turn-on Voltage (V)	^g CIE ^{EL}	^h CIE ^{PL}
PTNAA	-5.80	-3.54	2.26/2.37/2.41	13.7	9.6	23931	4.1	(0.54, 0.43)	(0.57, 0.38)

^{*a*}Highest Occupied Molecular Orbital.^{*b*}Lowest Unoccupied Molecular Orbital. ^{*c*}E^{*ele*}/E^{*opt*}, Electrochemical band gap/Optical band gap. ^{*d*} η_c^{max} , Luminous efficiency. ^{*e*} η_p^{max} , Power efficiency. ^{*f*}L^{max}, Maximum luminance. ^{*g*}CIE coordinates for EL. ^{*h*}CIE coordinates for PL.

Computational details:

The gas-phase density functional theory (DFT) calculations (B3LYP/ 6-31G* level) were carried out in order to gain a clear insight into the intramolecular charge transfer character of PTNAA at the molecular level and implemented in the Gaussian 09 package.^{S1-S3} All the optimized structures were identified by a frequency analysis and were shown to be all positive frequencies. On the principle of gas-phase optimized ground geometry, the absorption spectra in tetra hydro furan (THF) were calculated by the time-dependent density functional theory (TD-DFT) method which was employed to investigate ground to excited-state transitions using Gaussian 09 program along with B3LYP/6-31G* levels of theory.^{S4} The energy optimized structures (Fig. S12), adopted a bird-like structure.



Figure S16 Optimized geometry of PTNAA (bird-like structure) by using B3LYP/6-31G* level of theory.



Figure S17. Theoretically calculated absorption spectra of PTNAA Monomer at B3LYP/6-31G* level.

Table	S4	Summary	of the	excited	state	electronic	transitions	obtained	from	the	TD-DFT
calcula	ation	ns at the B3	SLYP/6	-31G* le	evel						

Model systems	States	Absorption (nm)	Energy (eV)	Oscillator strength (F)	Dominant contribution ^{<i>a</i>} (%)	Exp. (nm)
PTNAA	S1 S3	393 306	3.15 4.05	1.61 1.01	HOMO→LUMO (84%), H-1→L+1 (7%); H-2→LUMO (53%), H- 1→L+1 (28%);	328, 442
Co-polymer	S1 S3	396 318	3.13 3.90	2.51 1.06	HOMO→LUMO (73%), H-1→L+1 (8%); H-2→LUMO (32%), H- 1→L+1 (26%)	370
^H denotes HON	MO and L	denotes LUN	AO.			

References

S1. Lippert, E. Z. Naturforsch. A: Phys. Sci. 1955, 10, 541; (b) Mataga, N.; Kaifu, Y.; Koizumi,
M. Bull. Chem. Soc. Jpn. 1956, 29, 465.

S2. 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, Inc., Wallingford CT, 2009.

- S3. A. D. Becke, J. Chem. Phys. 1993, 98, 5648.
- S4. B. Lee, W.Yang, R. G. Parr, Phys. Rev. B 1988, 37, 785.
- S5. S. I. Gorelsky, SWizard Program (Version 4.6), University of Ottawa, Canada, 2007.