

Supplementary Information

Spectroscopic Characterization of Charge Transfer Complexes of TCNE with Aromatic Amines - The First Step of Tricyanovinilation Reaction

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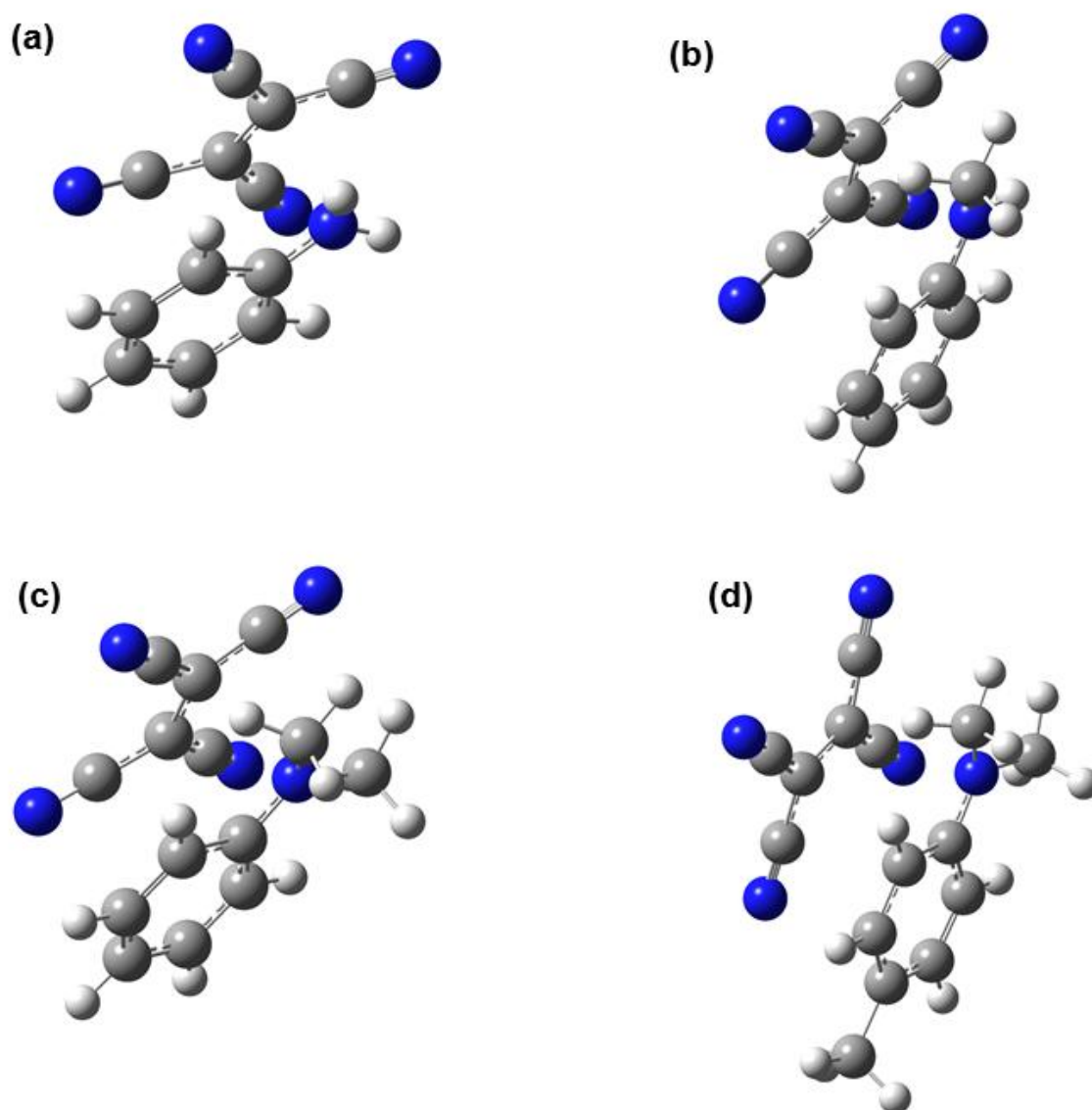


Figure S1. DFT optimized structures at B97D/6-311++G(3df,3dp) level of the charge transfer complexes of TCNE and (a) aniline, ANI, (b) *N*-methylaniline, NMA, (c) *N,N*-dimethylaniline, DMA, and (d) 4,*N,N*-trimethylaniline, TMA.

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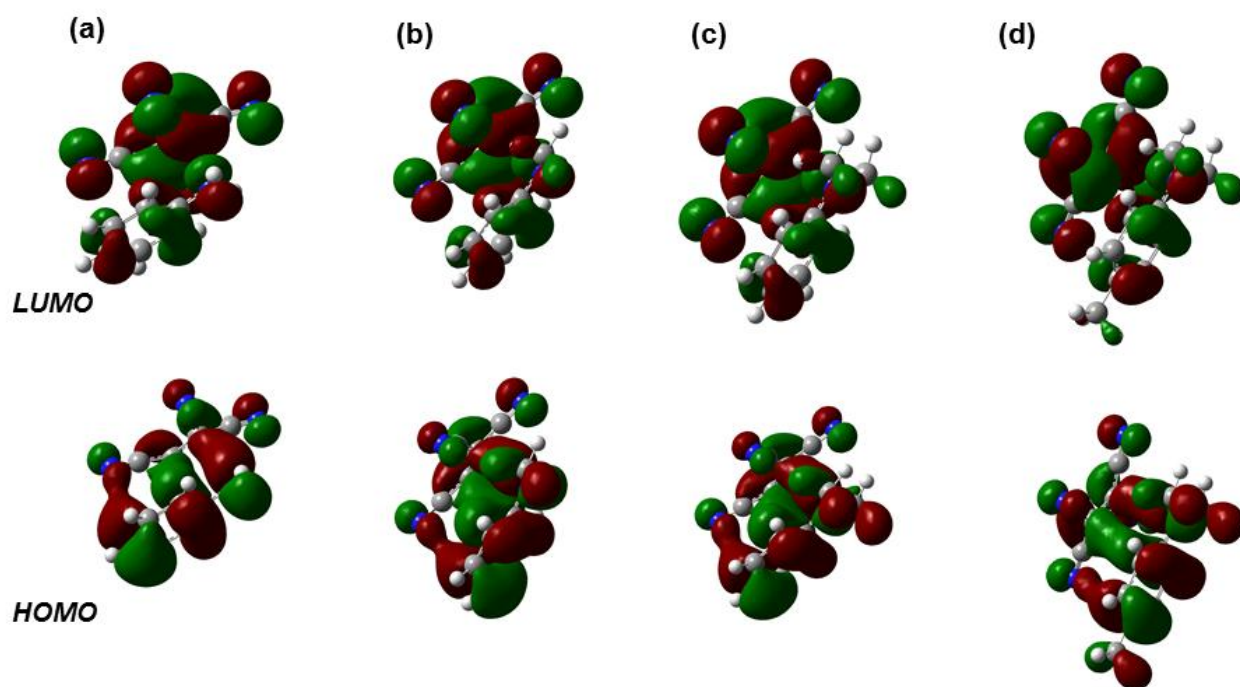


Figure S2. TDDFT HOMO and LUMO orbital contours obtained at B97D/6-311++G(3df,3dp) level for the charge transfer complexes of TCNE and (a) aniline, ANI, (b) *N*-methylaniline, NMA, (c) *N,N*-dimethylaniline, DMA, and (d) 4,*N,N*-trimethylaniline, TMA.

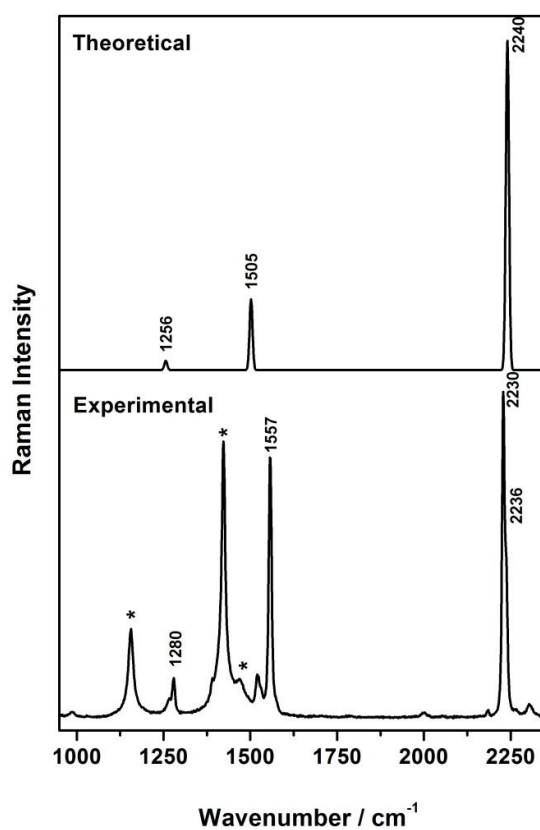


Figure S3. Experimental Raman spectrum of TCNE in dichloromethane (0.1 mol L^{-1}) obtained at $\lambda_0 = 404 \text{ nm}$ and theoretical Raman spectrum of TCNE obtained by DFT (B97D/6-311++G(3df,3dp) - SMD for dichloromethane).

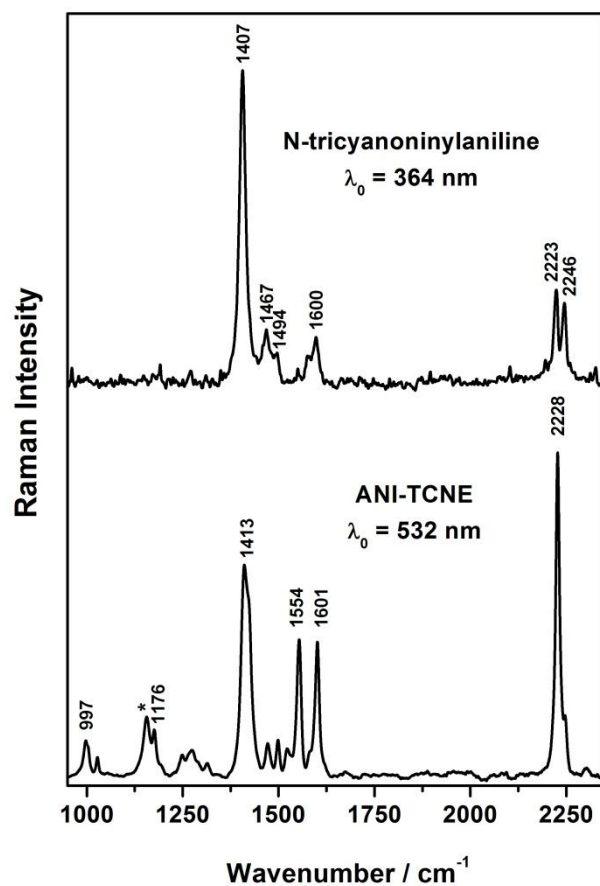


Figure S4. Raman spectrum of the ANI-TCNE charge transfer complex obtained at $\lambda_0 = 532$ nm, and the Raman spectrum of the respective tricyanovinilation product (*N*-tricyanovinylaniline) obtained at $\lambda_0 = 364$ nm in dichloromethane (0.1 mol L⁻¹).

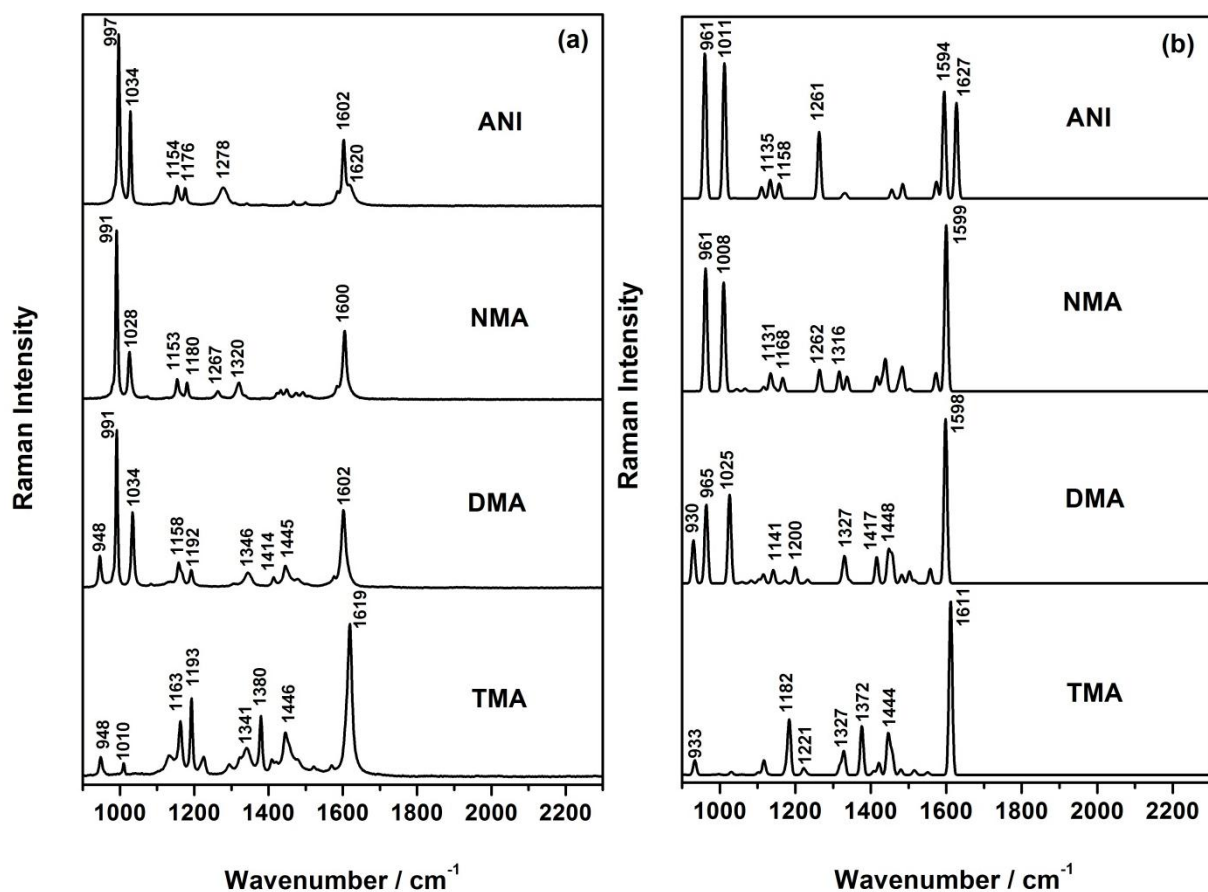


Figure S5. (a) Experimental Raman spectra obtained at $\lambda_0 = 1064$ nm and (b) DFT calculated Raman spectra at B97D/6-311++G(3df,3dp) level of aniline (ANI), *N*-methylaniline (NMA), *N,N*-dimethylaniline (DMA) and 4,*N,N*-trimethylaniline (TMA).

Table S1. Experimental and calculated Raman wavenumbers (cm^{-1}) for aromatic amines ANI, NMA, DMA and TMA and their respective vibrational assignments

	Experimental	Calculated	Assignment
ANI	997	961	Φ_{12}
	1034	1011	Φ_1
	1154	1135	Φ_{9b}
	1176	1158	Φ_{9a}
	1278	1261	$\Phi_{12}+\nu(\Phi-N)$
	1602	1594	Φ_{8a}
	1620	1627	$\delta(\text{NH}_2)$
NMA	991	961	Φ_{12}
	1028	1008	Φ_1
	1153	1131	Φ_{9b}
	1180	1168	Φ_{9a}
	1267	1262	$\Phi_{12}+\nu(\Phi-N)$
	1320	1316	$\Phi_3+\delta(\text{CH}_3)$
	1600	1599	Φ_{8a}
DMA	948	930	$\Phi_1+\nu(\text{N}(\text{CH}_3)_2)$
	991	965	Φ_{12}
	1034	1025	Φ_1
	1158	1141	Φ_{9b}
	1192	1200	$\Phi_{9a}+\nu(\Phi-N)$
	1346	1327	$\nu(\Phi-N)+\delta(\text{CH}_3)$
	1414	1417	$\delta(\text{CH}_3)$
	1445	1448	$\delta(\text{CH}_3)$
	1602	1598	Φ_{8a}
TMA	948	933	$\Phi_{10a}+\nu(\text{N}(\text{CH}_3)_2)$
	1163	1182	$\Phi_{9a}+\nu(\Phi-\text{CH}_3)$
	1193	1221	$\Phi_{12}+\nu(\Phi-\text{CH}_3)$
	1341	1327	$\nu(\Phi-N)+\delta(\text{CH}_3)$
	1380	1372	$\delta(\text{CH}_3)$
	1446	1444	$\delta(\text{CH}_3)$
	1619	1611	Φ_{8a}

ANI: aniline; NMA: *N*-methylaniline; DMA: *N,N*-dimethylaniline; TMA: 4, *N,N*-trimethylaniline.