Electronic Supplementary Information (ESI)

Plasmon-Enhanced Catalysis of Photo-Induced Charge Transfer from $TCNQF_4^-$ to $TCNQF_4^{2-}$

Jing Wang,[a] Weiqing Xu,[a] Jinxia Wu,[a] Guangtao Yu,[b] Xianghua Zhou,[a] and Shuping Xu[a*]

[a]State Key Laboratory of Supramolecular Structure and Materials, Jilin University, Changchun 130012, P. R. China

[b] State Key Laboratory of Theoretical and Computational Chemistry, Jilin University, 2 Liutiao Road, Changchun 130023, P. R. China.

*Corresponding author

Email: xusp@jlu.edu.cn

Tel: 86-431-85168505

Fax: 86-431-85193421

1. Experimental and Calculated Raman Spectra of $TCNQF_4$, Ag-$TCNQF_4$ and Ag_2-$TCNQF_4$.

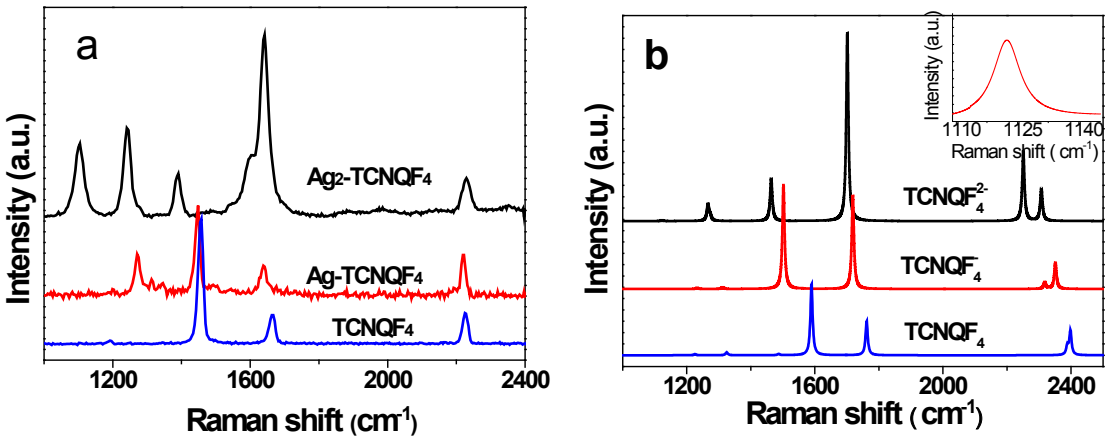

Figure S1. The Raman spectra of $TCNQF_4$, Ag-$TCNQF_4$ and Ag_2-$TCNQF_4$ from a) experiment and b) calculation. The insert shows the Raman vibration mode of $TCNQF_4^{2-}$ at 1122cm^{-1} by magnification.

Table S1. Raman shift assignments of $TCNQF_4^-$ and $TCNQF_4^{2-}$.

Raman shift (cm^{-1})						Assignment
$TCNQF_4$		$TCNQF_4^-$		$TCNQF_4^{2-}$(cm^{-1})		
Experiment	Calculation	Experiment	Calculation	Experiment	Calculation	
2226(m)	2398(m),2388(w)	2221(m)	2351(m),2317(m)	2207-2259(m)	2307(m), 2250(m)	ν C≡N, δ C≡N
1665(m)	1761(m)	1638(s)	1718(s)	1642(s)	1701(s)	ν C=C ring
1454(s)	1589(s)	1446(s)	1501(s)	1390(s)	1463(m)	ν C-CN wing
	1324(w)		1312(w)	1240(m)	1266(w)	νC6-C1-C7 deformation stretch
	1164(vw)		1145(vw)	1104(m)	1122(vw)	νC1-C2-C3 ring deformation stretch

To identify the Raman bands of Ag-$TCNQF_4$ and Ag_2-$TCNQF_4$, we took $TCNQF_4^-$ and $TCNQF_4^{2-}$ as models to compute the Raman spectra of Ag-$TCNQF_4$ and Ag_2-$TCNQF_4$, respectively, at the CAM-B3LYP method with the 6-311+G(d) basis set. For comparison, the Raman spectrum of $TCNQF_4$ was calculated. All the calculations were carried out by using the GAUSSIAN 09 program package.

The calculated Raman spectra are shown in Figure S1 of ESI. Via the comparison of experimental and calculated spectra, we can find that only very little band shifts appear, owing to simplified structure models we used and ideal medium surrounding settings. Most calculated and experimental Raman band positions are highly

coincident for both Ag-$TCNQF_4$ and Ag_2-$TCNQF_4$. So, we can infer that the product of the photo-induced charge transfer is Ag_2-$TCNQF_4$.