Resonance Raman spectroscopy and imaging of Franck-Condon vibrational activity and morphology in conjugated polymers for solar cells

John K. Grey

Department of Chemistry and Chemical Biology

University of New Mexico

Albuquerque, NM 87131

SUPPORTING INFORMATION

Table S1. Raman spectra fit parameters of aggregated and unaggregated P3HT limiting forms in PCBM blends. (Reproduced with permission from ref. [26], Copyright 2013 American Institute of Physics)

	unagg.		agg.	
mode (k)	$\hbar\omega_k$ (cm^{-1})	Δ_k [a]	$\hbar\omega_k$ (cm^{-1})	Δ_k [a]
ν_1	1518	0.70	1513	0.44
ν_2	1468	1.30	1447	1.18
ν_3	1372	0.61	1372	0.55
ν_4	1203	0.49	1204	0.30
ν_5	1173	0.55	1173	0.34
ν_6	1086	0.53	1086	0.27
ν_7	994	0.52	994	0.28
ν_8	723	0.51	723	0.39
$\nu_2+\nu_3$	2848	-	2832	-
$2\nu_2$ [b]	2927	-	2916	-
Γ (cm^{-1})	950		450	
$E_{0\text{-}0}$ (eV)	2.33		2.06	
$\hbar\omega_1$ (eV)	2.71		2.33	

[a] dimensionless units.

[b] Higher order overtones (0-3, etc.) are not included.

Table S2. P3DTV Raman vibrational modes and assignments and calculated displacements. (adapted from Ref. [27], Copyright 2018 Royal Society of Chemistry)

mode (k)	$\hbar\omega_k$ (cm^{-1})	Δ_k [a]	assignment [b]
ν_1	562	0.54	
ν_2	664	0.21	thienylene ring C-H wag

ν_3	913	0.27	vinyl C-H out-of-plane wag
ν_4	953	0.27	vinyl bend
ν_5	1047	0.2	thienylene C-H bend
ν_6	1088	0.2	
ν_7	1143	0.51	inter-ring C-C breathing modes
ν_8	1210	0.24	
ν_9	1278	0.67	vinyl C-H bend
ν_{10}	1390	0.87	thienylene ring C=C stretch
ν_{11}	1573	0.67	vinyl C=C stretch
	first overtone/combination region		
$\nu_3+\nu_{10}$	2315		
$\nu_7+\nu_9$	2430		
$\nu_6+\nu_{10}$	2490		
$2\nu_9$	2555		
$\nu_9+\nu_{10}$	2680		
$2\nu_{10}$	2790		
$\nu_9+\nu_{11}$	2855		
$\nu_{10}+\nu_{11}$	2970		
$2\nu_{11}$	3155		

[a] From time-dependent simulations of the Raman cross-correlation overlap function. Γ=380 cm^{-1}; $E_{0\text{-}0}$=14700 cm^{-1}. [b] Ref [37]

Table S3. Raman spectra fit parameters of PBTTT in PCBM blends. (adapted from ref. 44, Copyright 2014 American Chemical Society)

mode (k)	$\hbar\omega_k$ (cm^{-1})	Δ_k	Assignment
ν_1	1340	0.2	
ν_2	1365	0.2	

ν_3	1391	0.3	thiophene C-C stretch
ν_4	1415	0.5	thienothiophene C=C stretch
ν_5	1467	0.2	inter-ring thiophene C-C stretch
ν_6	1489	0.6	thiophene C=C stretch
ν_7	1500	0.7	
ν_8	1523	0.9	
ν_9	1563	0.7	
	2771		$2\nu_3$
	2804		$\nu_3+\nu_4$
	2831		$2\nu_4$
	2876		$\nu_4+\nu_5$
	2908		$\nu_4+\nu_6$
	2934		$2\nu_5$
	2977		$2\nu_6;\nu_5+\nu_7$
	3013		$\nu_6+\nu_8$

Γ=300 cm^{-1}(λ_{exc}=458 nm), Γ=550 cm^{-1}(λ_{exc}=568 nm) ; $E_{0\text{-}0}$=16130 cm^{-1}.

Table S4. Raman modes, relative intensities (I/I'), frequencies ($\hbar\omega$), displacements (Δ), and overtone and combination band assignments and frequencies of MDMO-PPV/DDQ and DNF blends. The letter k is an index referring to each fundamental transition in the Raman spectra. (adapted with permission from Ref. [27], Copyright 2018 Royal Society of Chemistry)

	DDQ			DNF		
mode (k)	$\hbar\omega_k$	$I_k/I_{k'}$	$\Delta_k{}^a$	$\hbar\omega_k$	$I_k/I_{k'}$	$\Delta_k{}^a$
ν_1	508	0.25	0.65	-		
ν_2	602	0.30	0.25	602	0.10	0.15
ν_3	800	0.08	0.15	-		

ν_4	974	0.13	0.38	967	0.03	0.30
ν_5	1044	0.08	0.30	-		
ν_6	1114	0.23	0.60	1110	0.22	0.40
ν_7	1210	0.11	0.15	1187	0.15	0.20
ν_8	1245	0.21	0.35	-		
ν_9	1280	0.68	1.02	1281	0.54	0.65
ν_{10}	1306	0.58	0.90	1309	0.37	0.72
ν_{11}	-			1340	0.08	0.05
ν_{12}	1410	0.13	0.20	1406	0.04	0.25
ν_{13}	1535	0.45	0.45	1548	0.26	0.40
ν_{14}	1568	1.00	0.85	1575	1.00	0.87
ν_{15}	1620	0.22	0.30	1620	0.05	0.20
$2\nu_6$	2192		(0.5)[b]	2190		
$\nu_6+\nu_{9,10}$[c]	2405			2400		
$2\nu_{9,10}$[c]	2582		(1.0)[b]	2575		(0.6)[b]
$\nu_6+\nu_{14}$	2690			2690		
$\nu_{9,10}$[c] $+\nu_{14}$	2852			2860		
$2\nu_{14}$	3136		(0.8)[b]	3160		(0.8)[b]
$2\nu_6+\nu_{9,10}$[c]	3475			-		
$3\nu_{9,10}$[c]	3855			-		
$2\nu_{9,10}$[c] $+\nu_{14}$	4138			4145		
$2\nu_{14}+\nu_{9,10}$[c]	4409			4450		
$3\nu_{14}$	4687			4730		
Γ (cm^{-1})			400			550

$E_{0\text{-}0}$ (cm^{-1})	16500	16950

[a] Generated from eqs. 1-4. The error in these values was found to be +/- 10%. [b] Estimated by comparing fundamental and overtone intensities. [c] Because of the small difference in frequencies between ν_9 and ν_{10} modes, we treat these as a collective mode in the overtone-combination bands, i.e., $\nu_{9,10}$.