

Electronic Supporting Information for

Resonance Raman study of the J-type aggregation process of a water soluble perylene bisimide

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S1. Computational Results

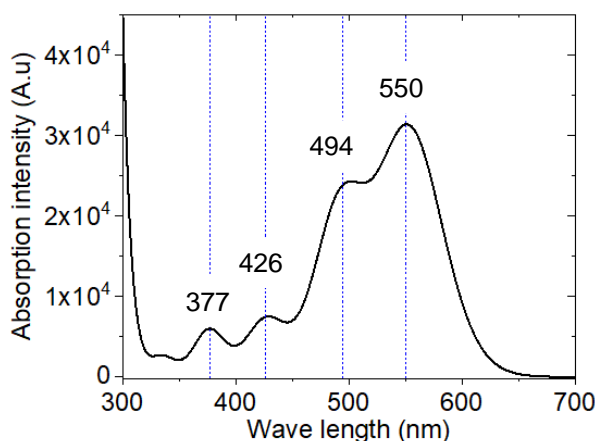
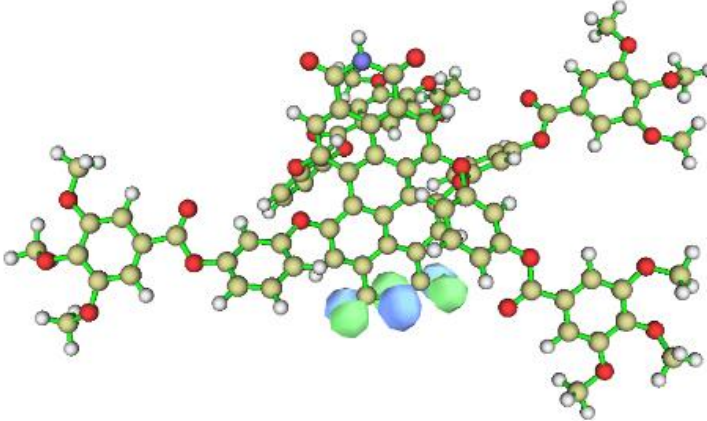
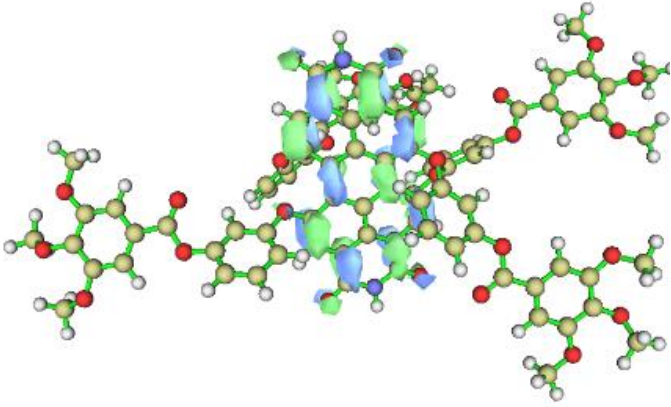
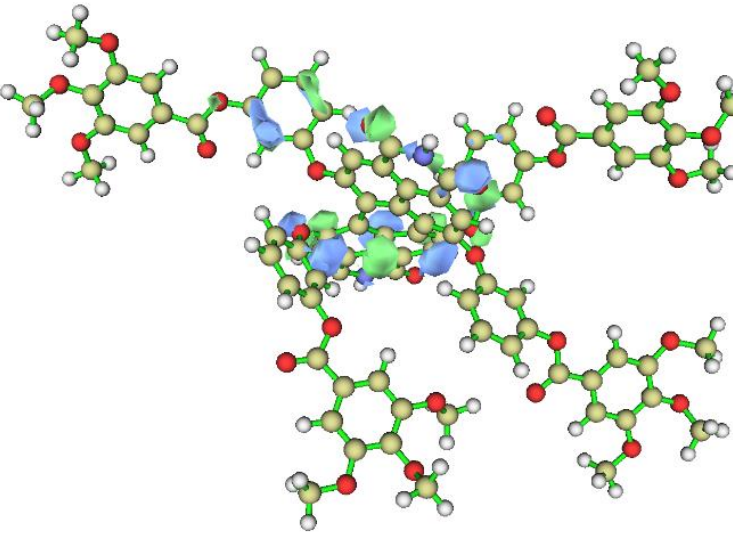
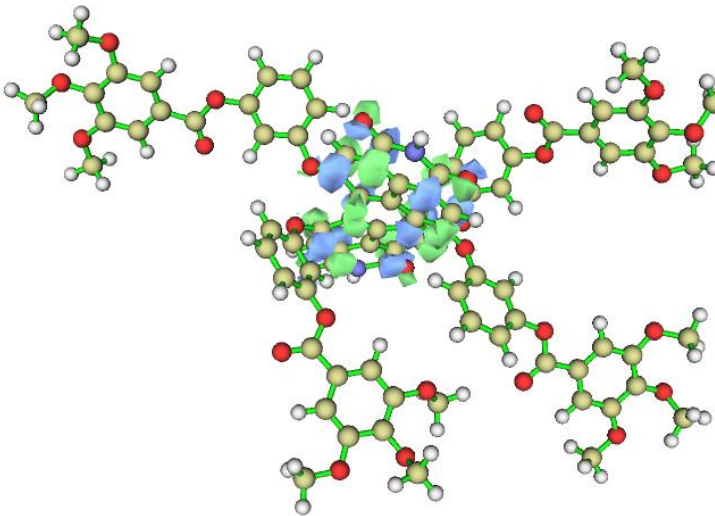
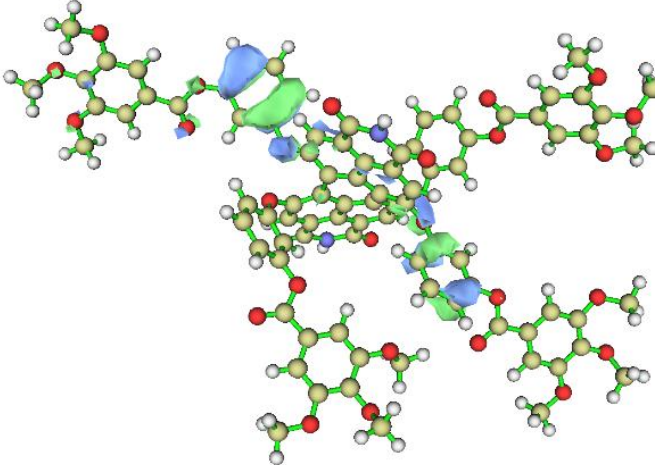
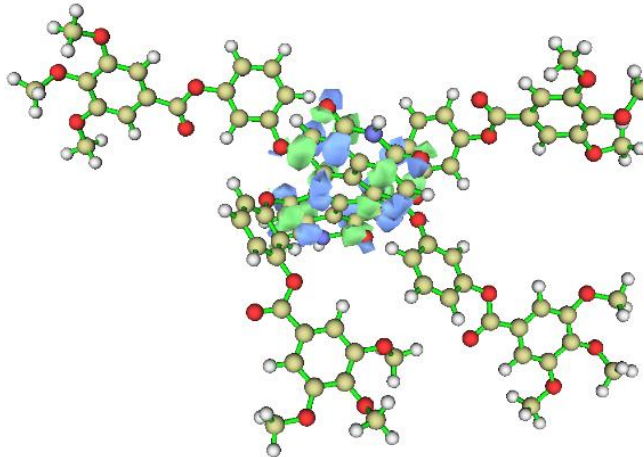
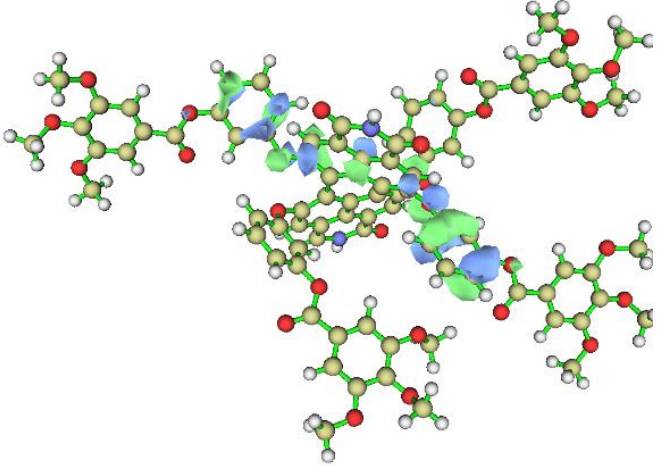
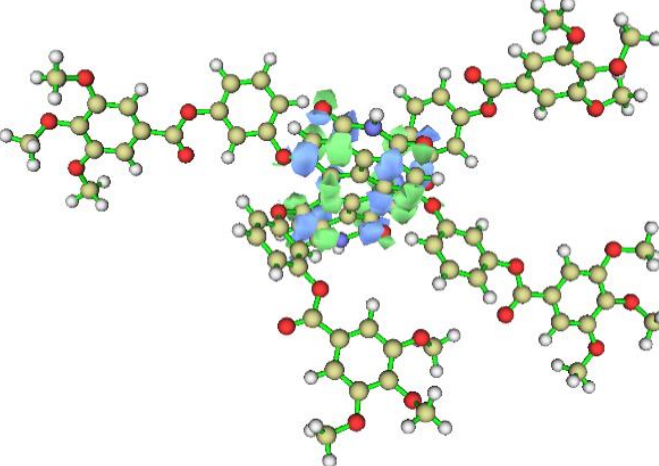


Fig. S1. Calculated UV-Vis absorption spectrum. Each vertical line represents a transition for which the hole and electron NTOs are pictured in Table S1.

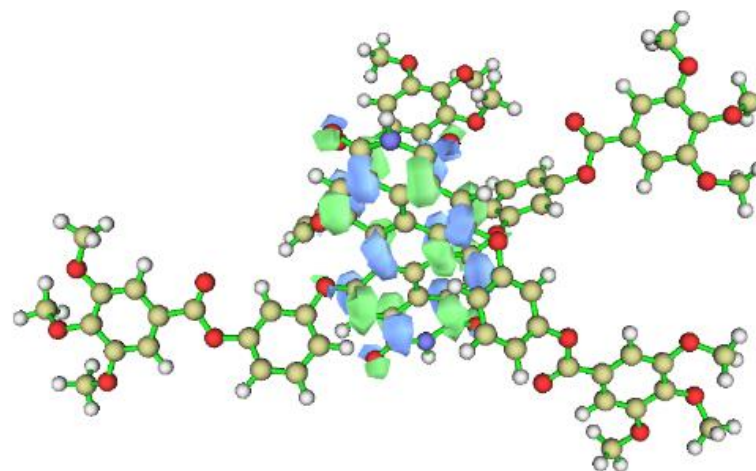
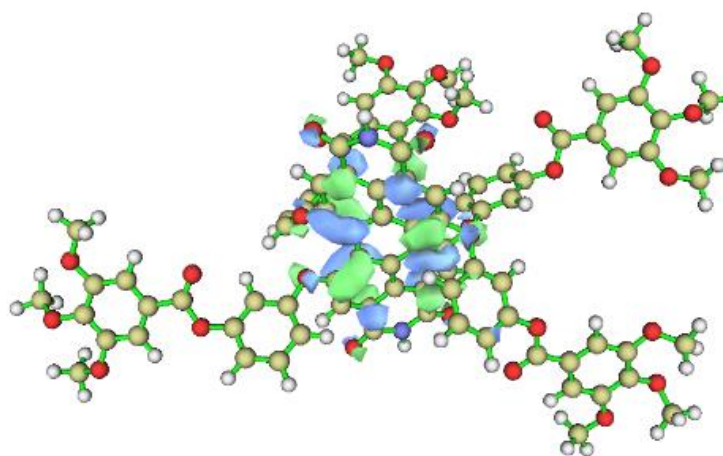
The TD-DFT calculations show two main absorption bands at ~530 and ~300 nm, in good agreement with the measured spectrum, see Fig 3 in the main text. Analysis of the natural transition orbitals (NTOs, see Table S1) shows that, while the lowest optically-allowed electronic excitation is confined over the core of the molecule as expected, the higher-lying transition involves a redistribution of the electron density from the outer imide moieties, where the hole NTO is localized, to the inner part of the molecule. Note the accidental symmetry breaking for the localized holes (a similar NTO confined over the other imine group is predicted at close energy).

Table S1. Hole and electron NTOs for the major electronic transitions of **MEG-PBI**.

λ (nm)	Hole NTO	Electron NTO
300		
377		

426		
494		

550



S1.2. Coordinates for optimized ground state structure

The energy minimum of **MEG-PBI** was calculated as neutral species (charge = 0 and multiplicity singlet).

Coordinates	X	Y	Z
C	-2.53473300	-1.75721400	-4.47654200
C	-2.63345300	-1.48336700	-3.03522100
C	-1.47076500	-1.18077100	-2.28371900
C	-0.19578700	-1.12031000	-2.90206400
C	-0.05027500	-1.37623700	-4.34166600
C	-3.87539500	-1.56486200	-2.40785600
C	-1.58924200	-0.92400500	-0.88037900
C	-2.88748200	-0.81514200	-0.29293300
C	-3.99970200	-1.27105100	-1.05490900
C	-0.40350600	-0.77000400	-0.07674100
C	0.82006000	-0.58318100	-0.77714700
C	0.92150600	-0.77104400	-2.14804000
H	1.87432900	-0.63903400	-2.64903100
H	-4.73451500	-1.86448400	-2.99635900
H	-1.16193000	-1.85254400	-5.99809700
C	-2.98209800	-0.29707700	1.05596300
C	-1.85100100	-0.46603400	1.91768100
C	-4.09732800	0.40774800	1.58535400
C	-0.56419500	-0.81391100	1.36564200
C	-2.00411500	-0.25812600	3.32947500
C	-4.22688000	0.64924500	2.94312700
C	0.40928400	-1.18280100	2.32555200
C	-0.93552700	-0.56912600	4.20804500
C	-3.22470500	0.25997500	3.83320600
C	0.25758900	-1.06988100	3.68865200
C	-1.07653900	-0.40294900	5.65882600
C	-3.40424700	0.47343100	5.27458600

H	1.05318100	-1.35127900	4.36981200
H	-2.42268300	0.24370100	7.06318200
O	-0.20605300	-0.68654300	6.47936100
O	-4.41531100	0.93238300	5.79581400
O	1.01497000	-1.34504300	-4.95269200
O	-3.48155100	-2.05007200	-5.19997500
O	1.68995300	-1.70384100	1.92195100
O	-5.08065900	0.92025200	0.75310000
O	1.96727400	-0.21058900	-0.08052300
O	-5.19294300	-1.39730400	-0.38846100
C	2.58625500	0.97408800	-0.43895700
C	3.97942800	0.99388600	-0.37036100
C	1.87392500	2.11838400	-0.80597500
C	4.65473300	2.17085600	-0.68052300
H	4.53143200	0.10238500	-0.09611400
C	2.57789200	3.28107000	-1.11632800
H	0.79094400	2.09792300	-0.84826500
C	3.97216400	3.32347900	-1.06523500
H	2.02780900	4.17323600	-1.39961300
H	4.51265900	4.22815300	-1.31036100
C	-4.81753400	2.08809700	0.06776900
C	-3.67005100	2.85628800	0.26221500
C	-5.79153100	2.49707400	-0.84993200
C	-3.50424000	4.03028300	-0.47524600
H	-2.90666600	2.56948000	0.97373000
C	-5.60209600	3.67711000	-1.56213000
H	-6.67636800	1.88531400	-0.98990200
C	-4.46023400	4.46640600	-1.39034900
H	-6.35857200	3.99381700	-2.27469200
H	-4.31410200	5.37344900	-1.95804400

C	-6.18083200	-2.26954700	-0.79803100
C	-5.92619400	-3.58755700	-1.18712200
C	-7.48843000	-1.79509200	-0.70006600
C	-7.00369400	-4.41708400	-1.49784700
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C	-8.54419900	-2.65015500	-1.00487500
H	-7.67289500	-0.77601200	-0.38084500
C	-8.32102800	-3.96472800	-1.41578000
H	-6.81349800	-5.44087000	-1.80721400
H	-9.15137000	-4.61684200	-1.65064800
C	1.87283700	-2.94605600	1.58657700
C	3.21465200	-3.28537400	1.25305100
C	0.83451300	-3.94790800	1.55580400
C	3.52025500	-4.57289400	0.89303500
H	3.97092000	-2.51268000	1.28436600
C	1.16816200	-5.22798300	1.18287800
H	-0.17614500	-3.67121400	1.81864200
C	2.49074000	-5.56706800	0.82972900
H	0.40433400	-5.99595200	1.14281800
H	2.73231000	-6.56710000	0.50289000
O	4.80840300	-4.80495900	0.52322300
O	-9.81116500	-2.07350600	-0.95813600
O	-2.34341800	4.73139200	-0.14473300
O	6.04817100	2.07993000	-0.68386000
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C	-10.87109000	-2.72775600	-0.38562200
C	6.82322700	3.04075400	-0.09624500
C	-1.63747400	5.48752500	-1.03502600
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C	-12.15046700	-0.65211700	-1.04417700

C	-13.26352000	-2.45869600	0.13386000
C	-13.34343100	0.08145800	-1.06448600
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C	8.73911600	1.65597200	-0.99691600
C	9.17335500	3.60889400	0.37663000
C	10.11399100	1.44259900	-1.12703500
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H	8.77216700	4.43378100	0.95084400
C	11.03290000	2.30143300	-0.49679100
C	-0.39033700	6.01552600	-0.41554100
C	-0.03919600	5.75616700	0.91097700
C	0.44352900	6.79631000	-1.23321100
C	1.15865300	6.26140100	1.42207100
H	-0.66945400	5.15500800	1.55375600
C	1.63699200	7.30585300	-0.72434200
H	0.12854100	6.98403900	-2.25181500
C	2.00926600	7.03053700	0.61277300

O	6.38247600	4.01070300	0.48303700
O	-1.97329700	5.69504600	-2.18170900
O	-10.79598100	-3.83063500	0.11083100
O	4.87726300	-6.94304600	1.31992600
O	9.20428600	-3.69547300	-1.18673600
O	10.84003100	-5.99813400	-0.85096800
O	9.78303600	-8.22663800	0.29540300
O	1.51201700	5.93143000	2.70523500
O	3.16304700	7.54471400	1.13832500
O	2.51795900	8.07119200	-1.43024600
O	10.49915900	0.33077800	-1.83290400
O	12.36563100	2.00092800	-0.56726500
O	11.49136900	4.14389400	0.89734700
O	-13.28246700	1.27494300	-1.72345100
O	-15.69447000	0.22281500	-0.60287100
O	-15.64050900	-2.20873800	0.60017300
C	-14.01245700	2.40521000	-1.24754800
H	-15.06072700	2.36755500	-1.55107300
H	-13.94962100	2.48695100	-0.15499300
H	-13.52646800	3.27486900	-1.69723000
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H	-16.63303200	-0.23418600	1.21328200
H	-15.68043500	1.28186100	1.20058100
H	-17.22373200	1.18762400	0.30518000
C	-15.66532100	-3.51887900	1.15002700
H	-15.00909400	-3.60135300	2.02580600
H	-16.69922500	-3.69321800	1.45303100
H	-15.37077200	-4.26970200	0.40627700
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H	10.04811000	-10.16560300	0.76987600
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H	11.87151300	-5.49816200	0.89729900
H	11.83699600	-7.24664700	0.50789400
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C	10.51035500	-3.17306900	-0.90758100
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H	10.45542000	-2.11035600	-1.15295800
C	11.05388200	5.20827100	1.73342000
H	10.42104000	4.83905000	2.54968600
H	11.96121800	5.65091400	2.14750100
H	10.50402400	5.96767800	1.16343300
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H	5.17745700	7.36108300	1.28838100

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N	-1.24214000	-1.67382700	-5.00272400

S2. UV Resonance Raman spectra in deuterated water

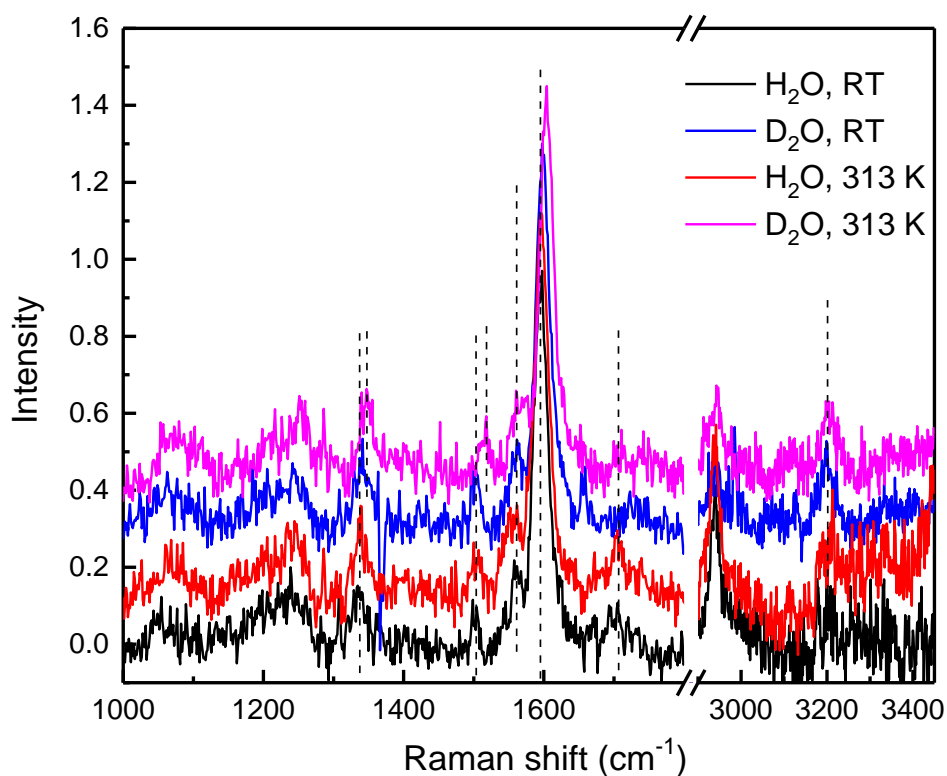


Fig. S2. RR spectra of **MEG-PBI** at 217 nm in water and deuterated water showing the amorphous phase at room temperature and the aggregate phase at 313 K.

UV Resonance Raman spectra of MEG-PBI at 217 nm show no dependence on isotopic substitution, suggesting that the bands observed are not related to exchangeable protons. Thus the bands observed in the high frequency region are associated with C-H stretching vibrations with no evidence for the N-H stretch expected in this region.

S3. RR spectral evolution with temperature in toluene

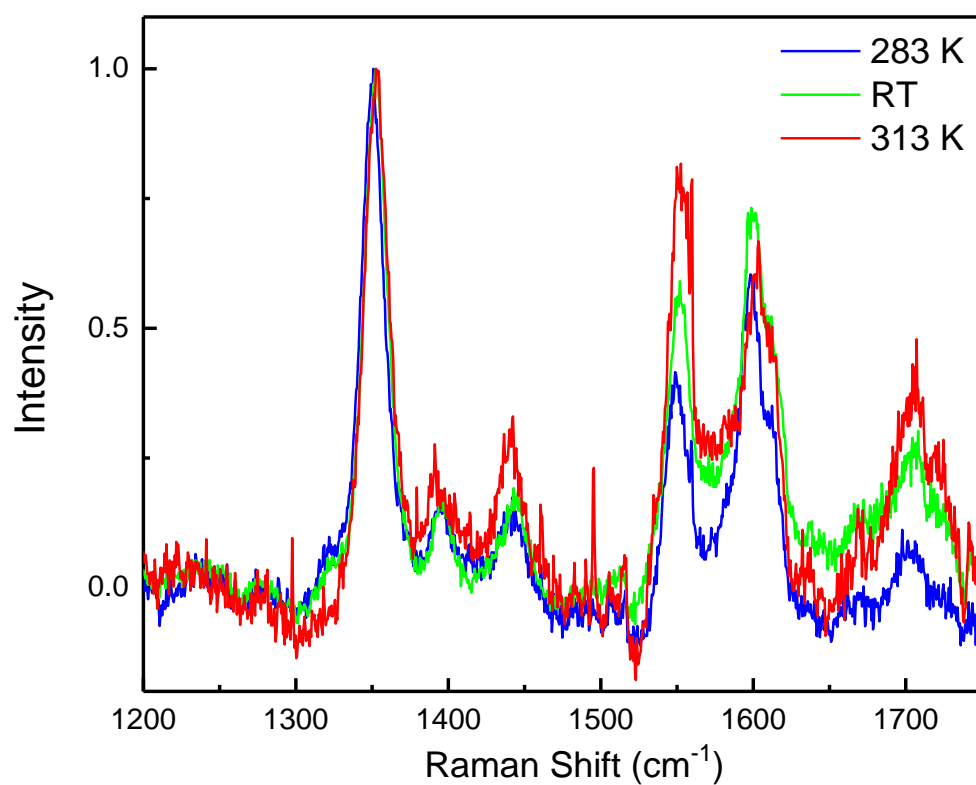


Fig. S3. Temperature-dependent RR spectra of **MEG-PBI** in toluene with excitation at 473 nm.

S4. Vibrational mode assignments

Table S2. Assignments of IR and Raman bands observed at 217, 282, 473 and 532 nm. Calculated wavenumbers were multiplied by a factor of 0.97.

IR Calc (cm ⁻¹)	Band Assignments	Raman Calc (cm ⁻¹)	RR 217 nm	RR 282 nm	RR 473 nm	RR 532 nm
1045	$\nu_{C=C}$, $\nu_{C=O}$, δ_{C-H} SC Breath mode phenyl ring PER	1048	1057 w	1057 m		
	δ_{C-H} SC	1180	1178 w	1178 m		
1199	δ_{N-H} PER δ_{C-H} SC	1202	1202 w	1202 w		1202 w
1243	$\nu_{C=C}$, δ_{C-H} , $\nu_{C=O}$ SC $\nu_{C=C}$, δ_{C-H} PER	1249	1240	1240		
1335	$\nu_{C=C} \parallel$ N-N axis, δ_{C-H} PER $\nu_{C=C}$, δ_{C-H} SC	1323	1333 w	1333 m		
1341	$\nu_{C=C} \parallel$ N-N axis PER	1341			1355 s	1355 s
1382	$\nu_{C=C}$, $\delta_{C-H} \perp$ N-N axis PER $\nu_{C=C}$, δ_{C-H} SC	1382			1395 m	1395 m
1381	δ_{N-H} PER	1381		1395 w		
	sym $\nu_{C=C}$ PER	1424		1447 vw	1447 m	1447 m
1472	δ_{C-H} phenyl rings SC	1489	1500 w	1500 m		
	$\nu_{C=C} \parallel$ N-N axis PER $\nu_{C=C}$, δ_{C-H} SC	1528	1553 w		1555 s	1555 s
1579 1594 1612	$\nu_{C=C}$, $\delta_{C-H} \perp$ N-N axis PER $\nu_{C=C}$, δ_{C-H} SC	1592 1613	1595 s	1595 s	1605 s	1605 m
1734 1754	$\nu_{C=O}$ imide PER $\nu_{C=O}$ esters SC	1737 1752	1729 w (esters)	1729 m (esters)	1706 w (free imide)	

Legend: ν : stretching, δ : bending, SC: side chains, PER: perylene ring, \parallel : parallel, \perp : perpendicular, sym: symmetric, w: weak, m: medium, s: strong.