

Supporting Information for

Stability and solid-state polymerization reactivity of imidazolyl- and benzimidazolyl-substituted diacetylenes: pivotal role of lattice water

Karim Fahsi,^a Jérôme Deschamps,^{§a} Kamel Chougrani,^{¶a} Lydie
Viau,^a Bruno Boury,^a André Vioux,^a Arie van der Lee^b
and Sylvain G. Dutremez^{*a}

^a*Institut Charles Gerhardt Montpellier, UMR 5253 CNRS-UM2-ENSCM-UM1, Equipe CMOS, Université Montpellier II, Bât. 17, CC 1701, Place Eugène Bataillon, 34095 Montpellier Cedex 5, France. E-mail: dutremez@univ-montp2.fr; Fax: +33-4-67-14-38-52; Tel: +33-4-67-14-42-23*

^b*Institut Européen des Membranes, CNRS - UMR 5635, Université Montpellier II, Case Courrier 047, Place Eugène Bataillon, 34095 Montpellier Cedex 5, France*

[§] Present address: Université Blaise Pascal, Institut de Chimie de Clermont-Ferrand, Groupe MO, BP 10448, 63000 Clermont-Ferrand, France.

[¶] Present address: Société Chryso, 7 rue de l'EUROPE, 45300 SERMAISES du Loiret, France.

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Results and discussion

Detailed description of the C-H \cdots O and C-H \cdots N hydrogen bonding interactions present in 1,6-bis(1-imidazolyl)-2,4-hexadiyne monohydrate (**2**)

The first hydrogen-bonding pattern has a geometry that resembles that of an acetylacetonate (acac) ligand in coordination chemistry. The C2-H fragment of the imidazolyl ring and the CH₂ group both point at the water molecule ($d(\text{H31}\cdots\text{O1}) = 2.756 \text{ \AA}$, $d(\text{C3}\cdots\text{O1}) = 3.559 \text{ \AA}$, $\angle\text{C3-H31}\cdots\text{O1} = 139.20^\circ$; $d(\text{H72}\cdots\text{O1}) = 2.478 \text{ \AA}$, $d(\text{C7}\cdots\text{O1}) = 3.426 \text{ \AA}$, $\angle\text{C7-H72}\cdots\text{O1} = 158.53^\circ$, see Table S1), and the H31, C3, N2, C7, and H72 atoms are nearly in the same plane (rms deviation of fitted atoms = 0.0067 \AA ; the angle between the H31-C3-N2 plane and the N2-C7-H72 plane is 2.33°). A survey of the Cambridge Structural Database (CSD)¹ indicates that this geometry is fairly common for hydrates possessing imidazole-CH₂ fragments. Also interesting in the case of **2** is the fact that the strongest C-H \cdots O interactions are CH₂ \cdots O interactions and not those involving imidazolyl hydrogens. This observation is counterintuitive on the basis of $\text{p}K_{\text{a}}$ values: the experimentally determined $\text{p}K_{\text{a}}$ value of the C2-H proton of 1-methylimidazole is 33.1 (theoretically determined $\text{p}K_{\text{a}} = 35.1$),² and the $\text{p}K_{\text{a}}$ value of methane is 48.³ Yet, the situation is not unusual and, for a number of non-ionic compounds (i.e. not imidazoliums and not *N*-oxides) for which the imidazole part and the CH₂ group interact with the same water molecule, it is observed that CH₂ \cdots OH₂ interactions are stronger than C2-H \cdots OH₂ interactions (Table S2).

The second hydrogen-bonding pattern is quite different from the first one. In this case, the C5-H fragment of the imidazolyl ring (see generic numbering scheme in Scheme 3) interacts with the water molecule ($d(\text{H61}\cdots\text{O1}) = 2.509 \text{ \AA}$, $d(\text{C6}\cdots\text{O1}) = 3.341 \text{ \AA}$, $\angle\text{C6-H61}\cdots\text{O1} = 143.53^\circ$, see Table S1), and the CH₂ group interacts with a nearby imidazolyl nitrogen ($d(\text{H71}\cdots\text{N4}) = 2.590 \text{ \AA}$, $d(\text{C7}\cdots\text{N4}) = 3.529 \text{ \AA}$, $\angle\text{C7-H71}\cdots\text{N4} = 160.15^\circ$). Owing to the fact that the C6-H61 and C7-H71 bonds interact with different hydrogen-bond acceptors, the H61, C6, N2, C7, and H71 atoms do not lie in the same plane (rms deviation of fitted atoms = 0.2094 \AA ; the angle between the H61-C6-N2 plane and the N2-C7-H71 plane is 22.06°). It is also noteworthy that the C5-H \cdots OH₂ interactions observed in this second hydrogen-bonding pattern are much stronger than the C2-H \cdots OH₂ interactions observed in the first one. Interestingly, a similar situation is observed in the X-ray crystal structure of tetrakis(1H-imidazol-1-ylmethyl)methane pentahydrate (refcode PUNCAD in Tables S2 and S3):⁴ C5-H \cdots OH₂ distances are, on the average, shorter than C2-H \cdots OH₂ distances. This

phenomenon cannot be ascribed to a difference in pK_a values between C5-H and C2-H as the two protons have identical pK_a values (theoretically determined pK_a values = 35.1).² Presumably, crystal packing forces and/or geometrical constraints are responsible for this situation.

Detailed description of the $\pi\cdots\pi$ and C-H $\cdots\pi$ interactions present in 1,6-bis(1-benzimidazolyl)-2,4-hexadiyne (**5**)

There are two types of $\pi\cdots\pi$ interactions in **5**. In the first type (Figure S1), the interacting benzimidazole rings are parallel with an offset distance of 1.838 Å. Interaction between the benzimidazolyl groups takes place through the imidazole fragments. The perpendicular distance between the imidazole rings is 3.347 Å, the Cg \cdots Cg distance (Cg is the centroid position of the imidazolyl ring) is 3.819 Å, and the angle between the Cg-Cg vector and the normal to the imidazolyl ring is 28.8°. These parameters are comparable to those found for metal complexes with pyridine-based ligands.⁵ A survey of the Cambridge Structural Database (CSD)¹ revealed eleven single-component, non-ionic, benzimidazole-based compounds with a Cg \cdots Cg distance smaller than 4.0 Å: the minimum value was 3.381 Å, the maximum value 3.817 Å, and the mean distance 3.569 Å. Thus, the $\pi\cdots\pi$ interaction observed in **5** does not seem to be very strong.

This intermolecular $\pi\cdots\pi$ interaction is supplemented by two symmetrical C-H $\cdots\pi$ interactions (Figure S1). The C-H bonds are those of methylene groups and the π clouds belong to imidazolyl fragments. The geometrical parameters for these identical interactions are: $d(\text{H152}\cdots\text{Cg}) = 2.971$ Å, $d(\text{C15}\cdots\text{Cg}) = 3.470$ Å, and $\angle\text{C15-H152}\cdots\text{Cg} = 112.68^\circ$. A survey of the Cambridge Structural Database (CSD)¹ revealed eighty-seven benzimidazole-based compounds with a CH₂ \cdots Cg distance smaller than 4.0 Å: the minimum H \cdots Cg value was 2.590 Å, the maximum value 4.000 Å, and the mean distance 3.590 Å. Thus, the CH₂ $\cdots\pi$ interactions observed in **5** appear to be reasonably strong. The H151 hydrogen borne by the C15 methylene carbon is probably also involved in a C-H $\cdots\pi$ interaction with the phenyl part of the same benzimidazolyl group that H152 is interacting with (see Figure S1). The geometrical parameters indicate, however, that this interaction is weaker than the H152 \cdots imidazolyl interaction: $d(\text{H151}\cdots\text{Cg}) = 3.134$ Å, $d(\text{C15}\cdots\text{Cg}) = 3.693$ Å, and $\angle\text{C15-H151}\cdots\text{Cg} = 117.73^\circ$ (Cg is the centroid position of the phenyl part of the benzimidazolyl moiety).

The second $\pi\cdots\pi$ interaction is shown in Figure S2. It is orthogonal to the first one. As already observed in the first $\pi\cdots\pi$ interaction, this second $\pi\cdots\pi$ interaction involves the imidazole fragments from two facing benzimidazolyl groups. The interacting benzimidazole rings are parallel with an offset distance of 1.352 Å; the perpendicular distance between the imidazole rings is 3.295 Å, the Cg \cdots Cg distance 3.562 Å, and the angle between the Cg-Cg vector and the normal to the imidazolyl ring is 22.3°. This second interaction is definitely stronger than the first one.

This second intermolecular $\pi\cdots\pi$ interaction is supplemented by two symmetrical edge-on interactions (Figure S2). In each edge-on interaction, the phenyl part of a benzimidazole moiety interacts with the phenyl centroid and the imidazolyl centroid of a nearby benzimidazole moiety. The geometrical parameters for these edge-on interactions are: $d(\text{H81}\cdots\text{Cg}) = 3.137$ Å, $d(\text{C8}\cdots\text{Cg}) = 3.808$ Å, and $\angle\text{C8-H81}\cdots\text{Cg} = 130.96^\circ$; $d(\text{H71}\cdots\text{Cg}) = 2.857$ Å, $d(\text{C7}\cdots\text{Cg}) = 3.767$ Å, and $\angle\text{C7-H71}\cdots\text{Cg} = 163.86^\circ$. A survey of the Cambridge Structural Database (CSD)¹ revealed five uncomplexed benzimidazole-based compounds for which a similar situation is observed in the solid state (refcodes QAYQIR, RUFBW01, SURLUN, YORLEW, and WAJBOA). For these compounds, the minimum C_{phenyl}-H \cdots Cg(phenyl) value was 2.879 Å, the maximum value 3.478 Å, and the mean distance 3.291 Å. For the C_{phenyl}-H \cdots Cg(imidazole) interaction, the minimum H \cdots Cg value was 2.966 Å, the maximum value 3.322 Å, and the mean distance 3.075 Å. Thus, the edge-on interactions observed in **5** are fairly strong.

References

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Tables

Table S1. Geometrical parameters for the hydrogen-bonding interactions involving the water molecule in solvate **2**.

interaction ^a	distance/Å			angle/deg
	D-H	H...A	D...A	D-H...A
O1-H11 ⁱ ...N4 ^{iv}	0.869	1.986	2.853	175.69
O1-H11...N4 ^v	0.869	1.986	2.853	175.69
C3 ⁱⁱ -H31 ⁱⁱ ...O1	0.984	2.756	3.559	139.20
C3 ⁱⁱⁱ -H31 ⁱⁱⁱ ...O1	0.984	2.756	3.559	139.20
C6-H61...O1	0.972	2.509	3.341	143.53
C6 ⁱ -H61 ⁱ ...O1	0.972	2.509	3.341	143.53
C7 ⁱⁱ -H72 ⁱⁱ ...O1	0.998	2.478	3.426	158.53
C7 ⁱⁱⁱ -H72 ⁱⁱⁱ ...O1	0.998	2.478	3.426	158.53

^a Symmetry codes: (i) $2 - x, y, 3/2 - z$; (ii) $1/2 + x, 1/2 - y, 1 - z$; (iii) $3/2 - x, 1/2 - y, 1/2 + z$; (iv) $1/2 + x, -1/2 + y, 3/2 - z$; (v) $3/2 - x, -1/2 + y, z$.

Table S2. CH₂...OH₂ and C2-H...OH₂ distances found in the CSD for hydrates possessing non-ionic imidazole-CH₂ fragments for which the CH₂ and C2-H parts both interact with the same water molecule.

refcode	distance/Å	
	CH ₂ ...OH ₂	C2-H...OH ₂
BEHBIA	2.827	2.587
DAYQOK	2.852	2.462
DUDCEL	2.548	2.963
ESEMAQ	2.852	2.552
KUQYOL	2.474	2.657
LORTUI	2.574	2.677
OFAXEZ	2.828	2.625
TAVNUA	2.750	2.849
PUNCAD ^a	2.972	2.504
PUNCAD ^b	3.089	2.687
PUNCAD ^c	2.679	2.584
PUPHAK	2.573	2.635

^a Fragment 1. ^b Fragment 2. ^c Fragment 3.

Table S3. C5-H...OH₂ distances found in the CSD for hydrates possessing non-ionic imidazole-CH₂ fragments.

refcode	distance/Å
	C5-H...OH ₂
AHIMUA	2.716
GUHRAC	2.619
SANQOO	2.586
TALVUY	2.523
TISKEM	2.652
PUNCAD ^a	2.532
PUNCAD ^b	2.348
RUVDUI	2.688

^a Fragment 1. ^b Fragment 2.

Figures

Figure S1. Close-up view showing one $\pi\cdots\pi$ interaction assisted by two $\text{CH}_2\cdots\pi$ interactions in a polymeric chain of **5**.

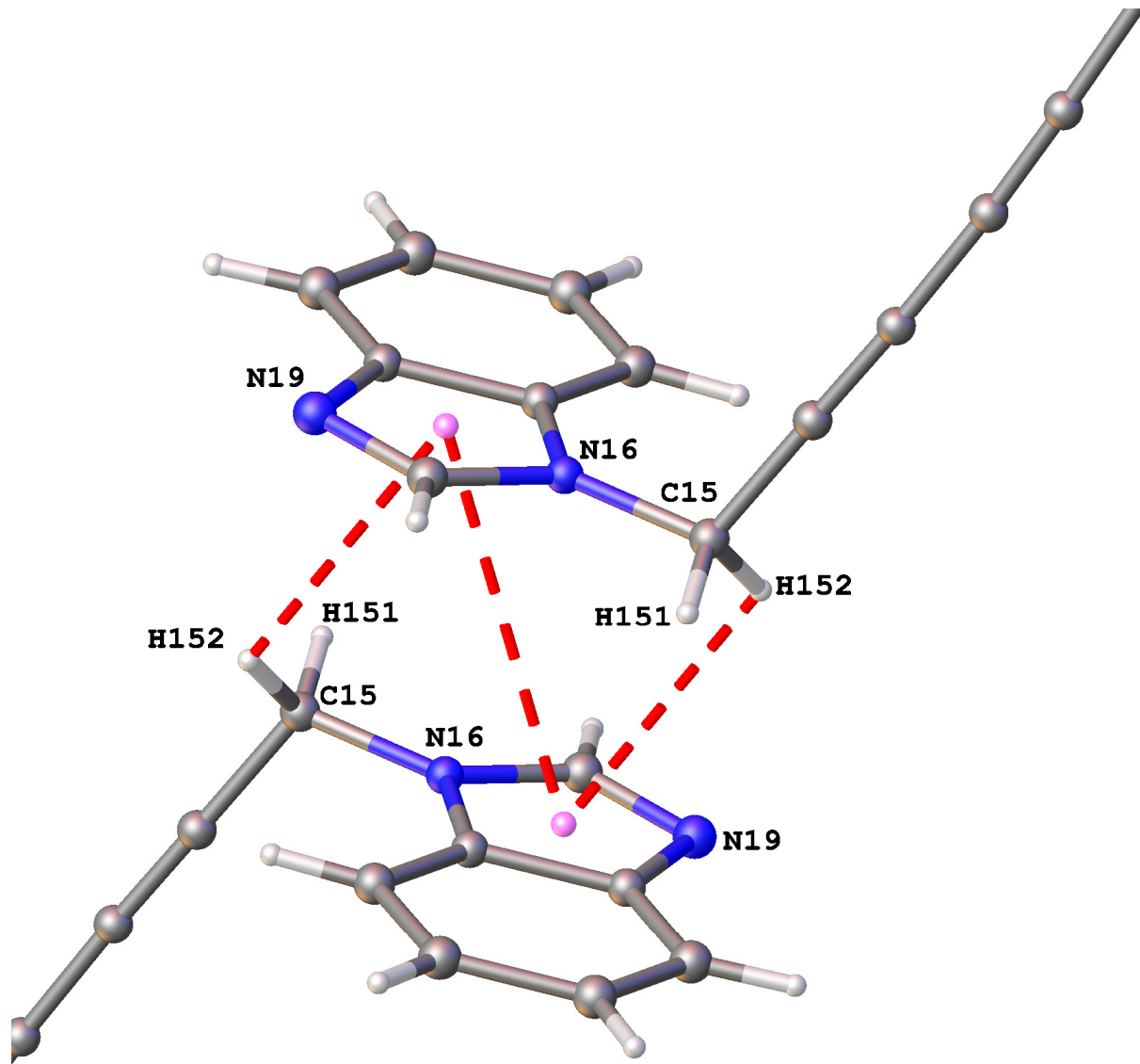


Figure S2. Close-up view showing one $\pi \cdots \pi$ interaction assisted by two edge-on interactions in a polymeric chain of **5**.

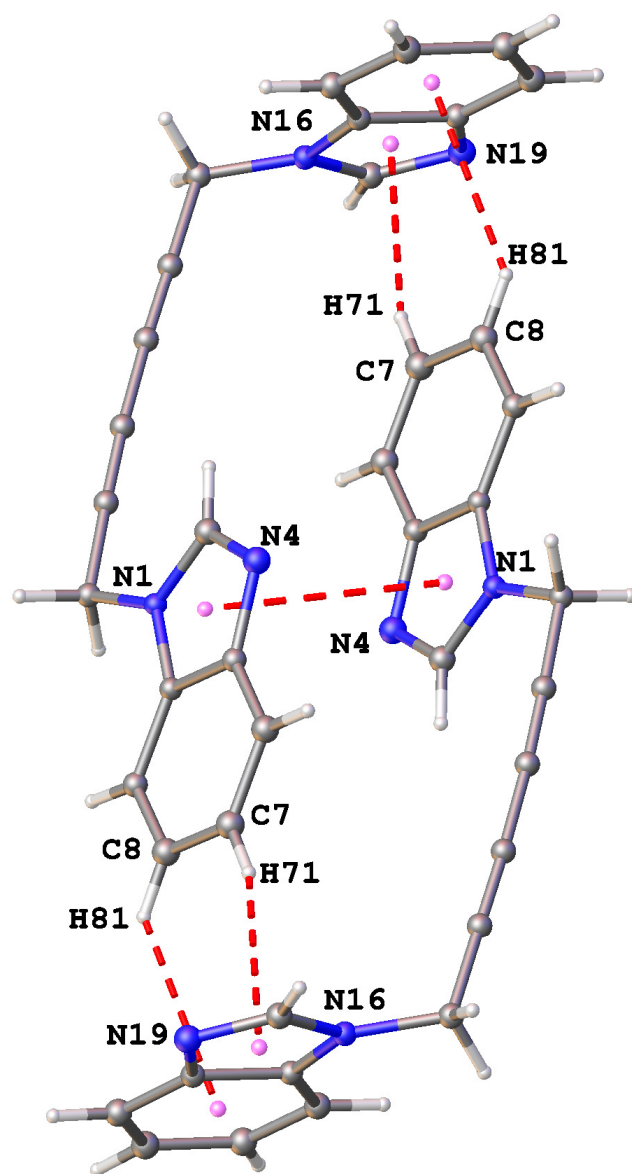


Figure S3. TGA (red) and DSC (blue) curves recorded during the thermolysis of **2** at 450 °C.

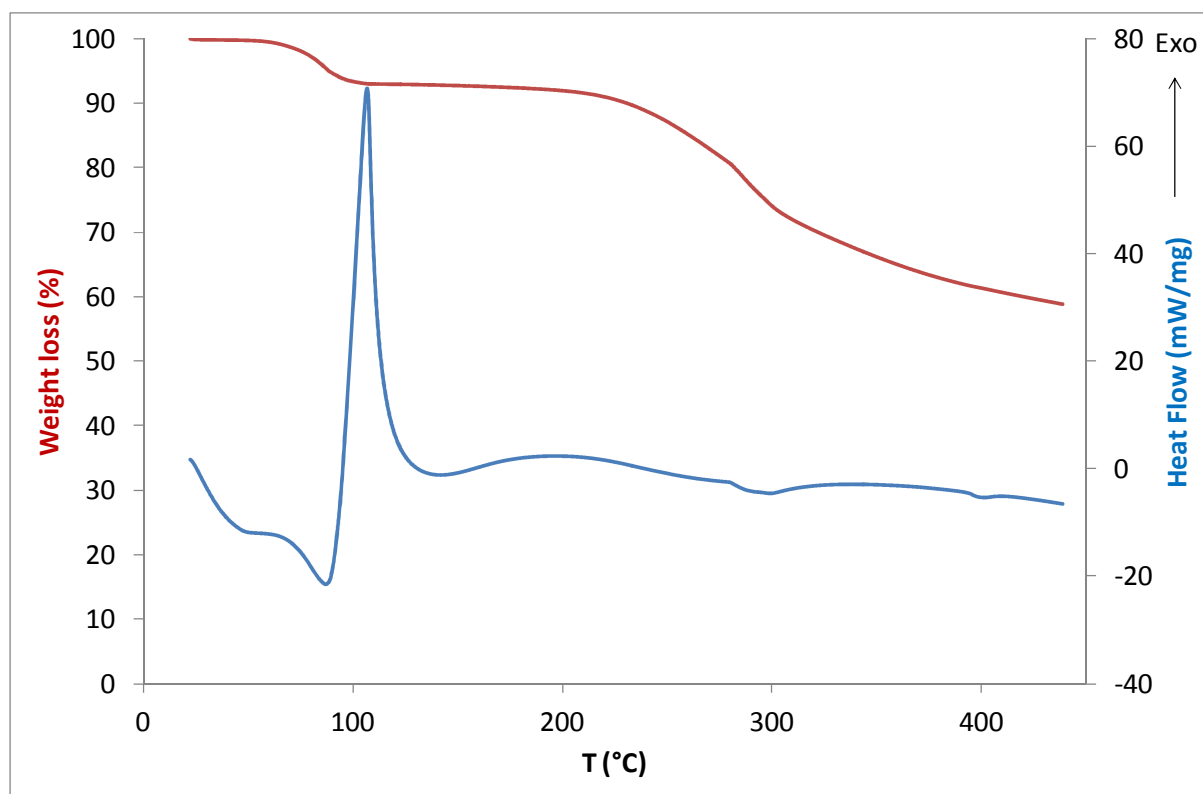


Figure S4. Raman spectra of **4** and poly-**4**.

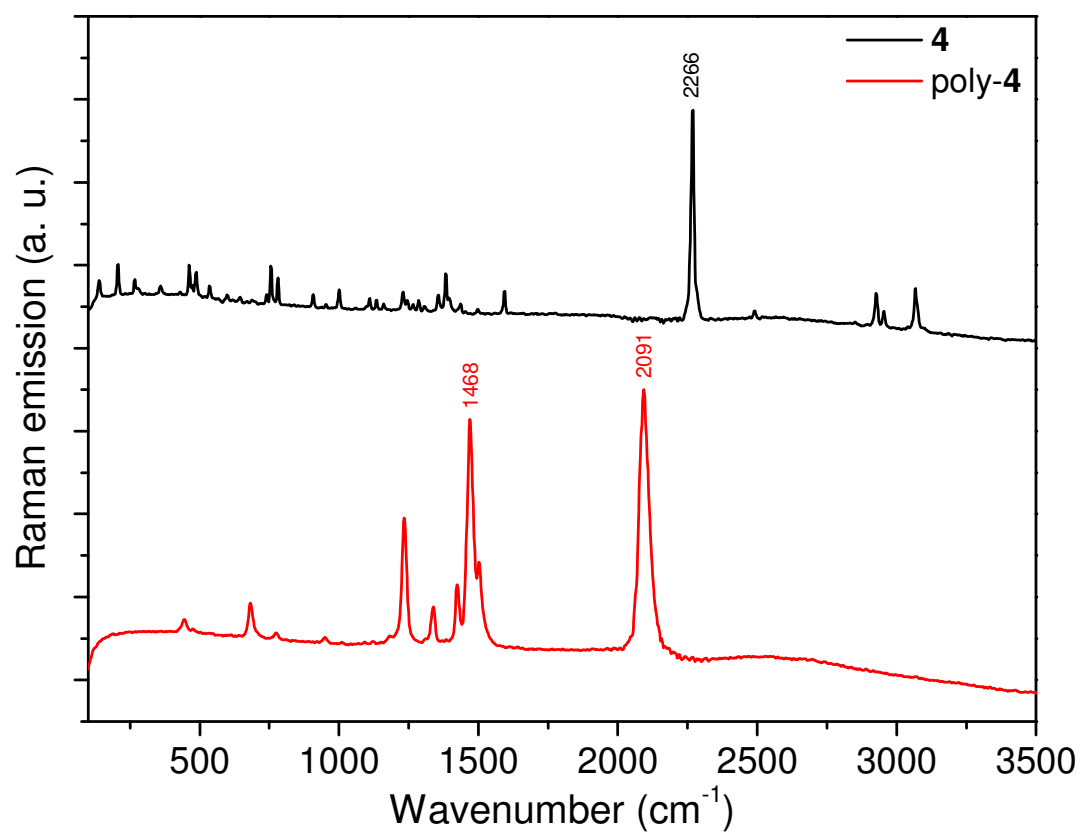


Figure S5. UV-vis absorption spectra of **4** and poly-**4**.

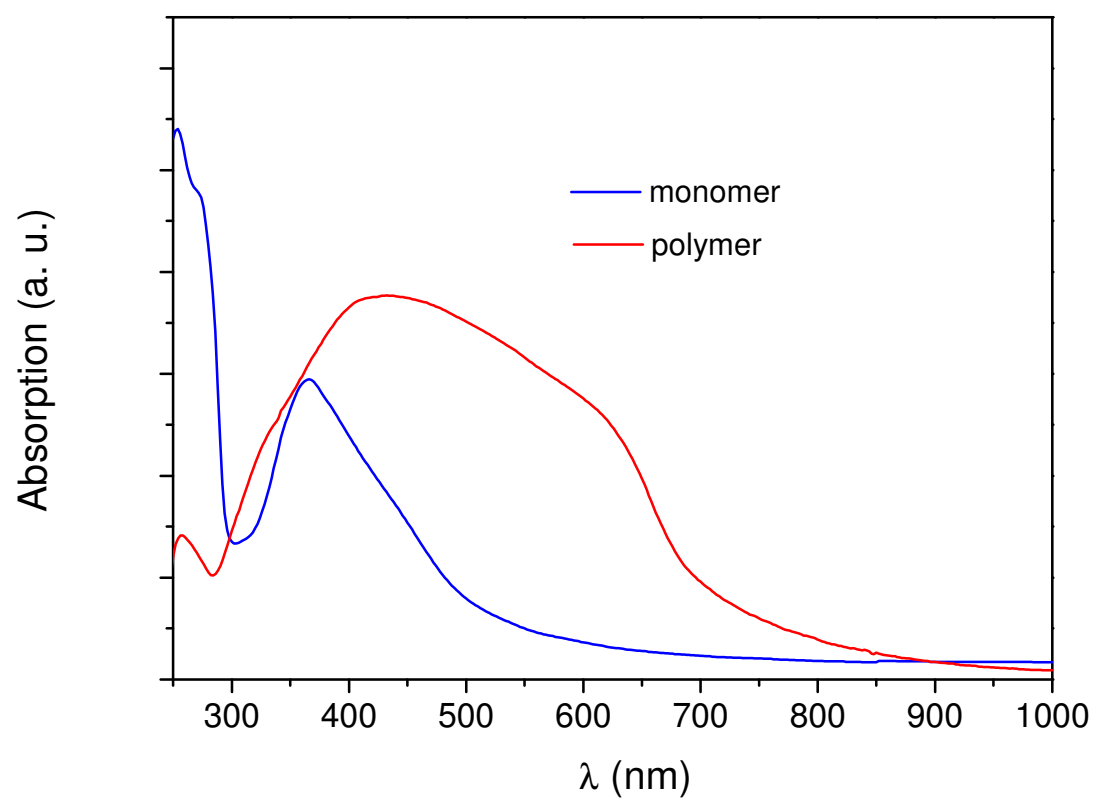


Figure S6. Infrared spectra of **4**, unwashed poly-**4**, and washed poly-**4**.

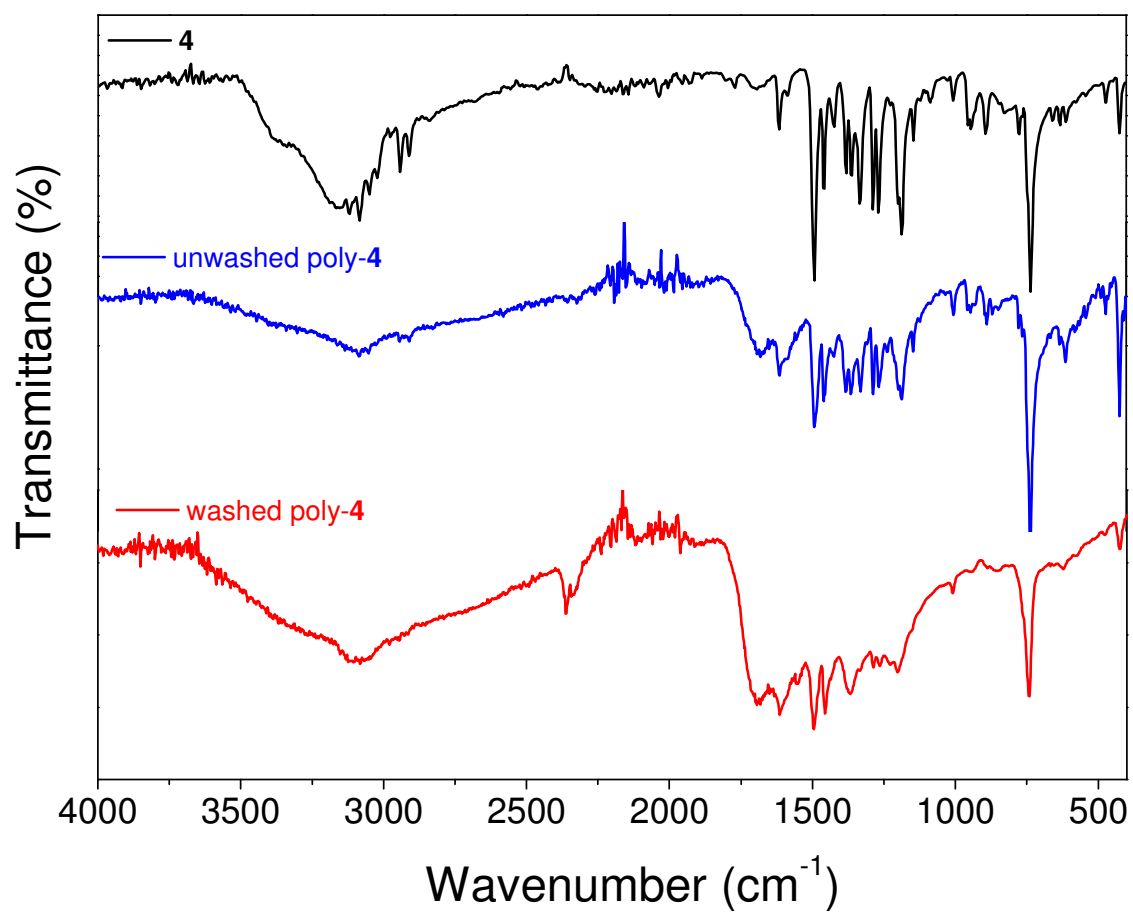


Figure S7. XRPD data of **4**: observed (red), calculated (blue), and residual (black) profiles.

