Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

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Combined SERS/DFT studies of push-pull chromophores self-assembled monolayers: insights of their surface orientation.

V. Gadenne,[b,c*] B. Grenier,[a] C. Praveen,[a] P. Marsal,[a] J. C. Valmalette,[b,d] L. Patrone,[b,c] J. M. Raimundo [a*]

[a]Aix Marseille Univ., CNRS, CINaM UMR 7325, Campus de Luminy, Case 913, 13288 Marseille Cedex 09, France.
[b]Aix Marseille Univ., Université de Toulon, CNRS, IM2NP UMR 7334, Campus de St Jérôme, 13397 Marseille Cedex 20, France.
[c]Aix Marseille Univ., Université de Toulon, CNRS, IM2NP UMR 7334, Yncréa Méditerranée, ISEN Toulon, Maison du Numérique et de l'Innovation, Place G. Pompidou, 83000 Toulon, France.
[d]Université du Sud-Toulon-Var, CNRS, IM2NP UMR 7334, Bâtiment R, BP 20132, 83957 La Garde Cedex, France.

Email: virginie.gadenne@yncrea.fr; jean-manuel.raimundo@univ-amu.fr

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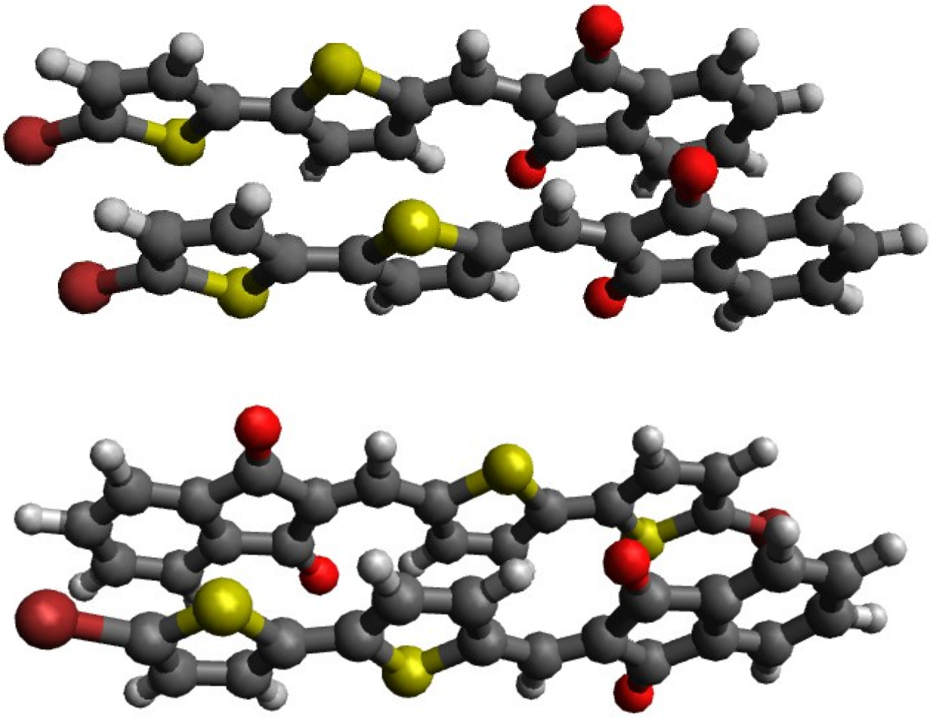
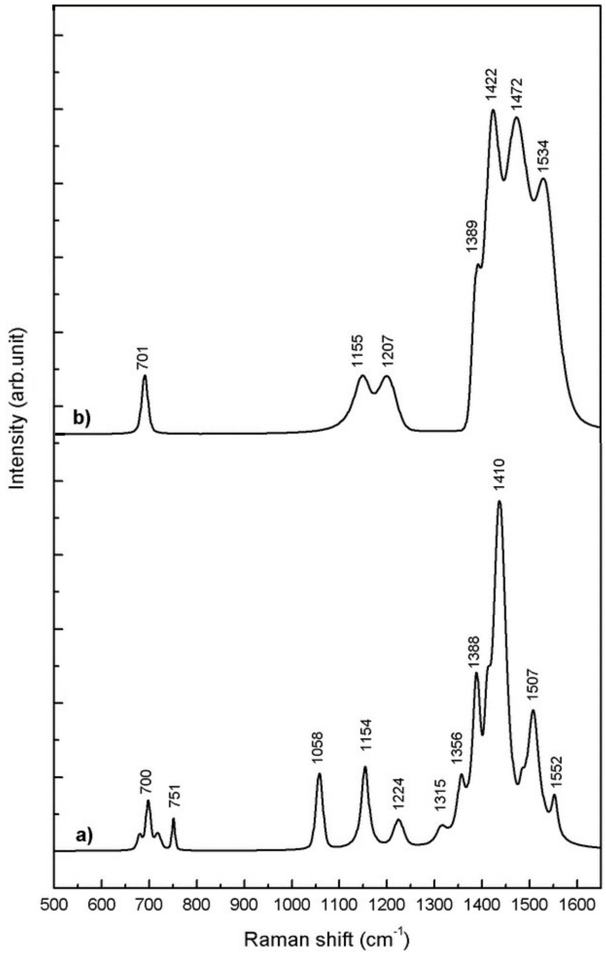
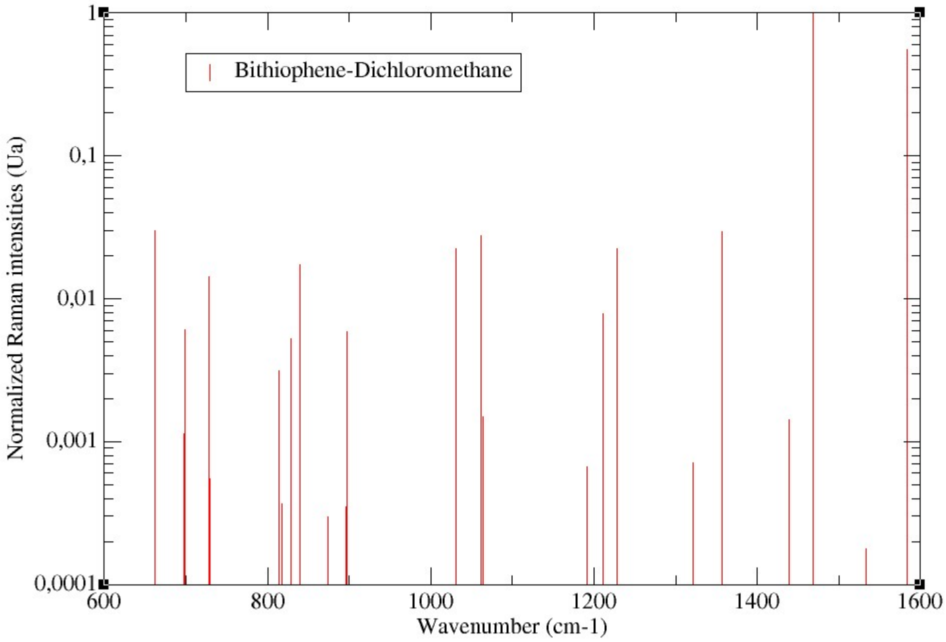
1- Figure S1: Parallel (top) and antiparallel (down) dimers geometries of **T_2-Id** obtained after M062X/6-31(d,p) calculations in dichloromethane using CPCM model



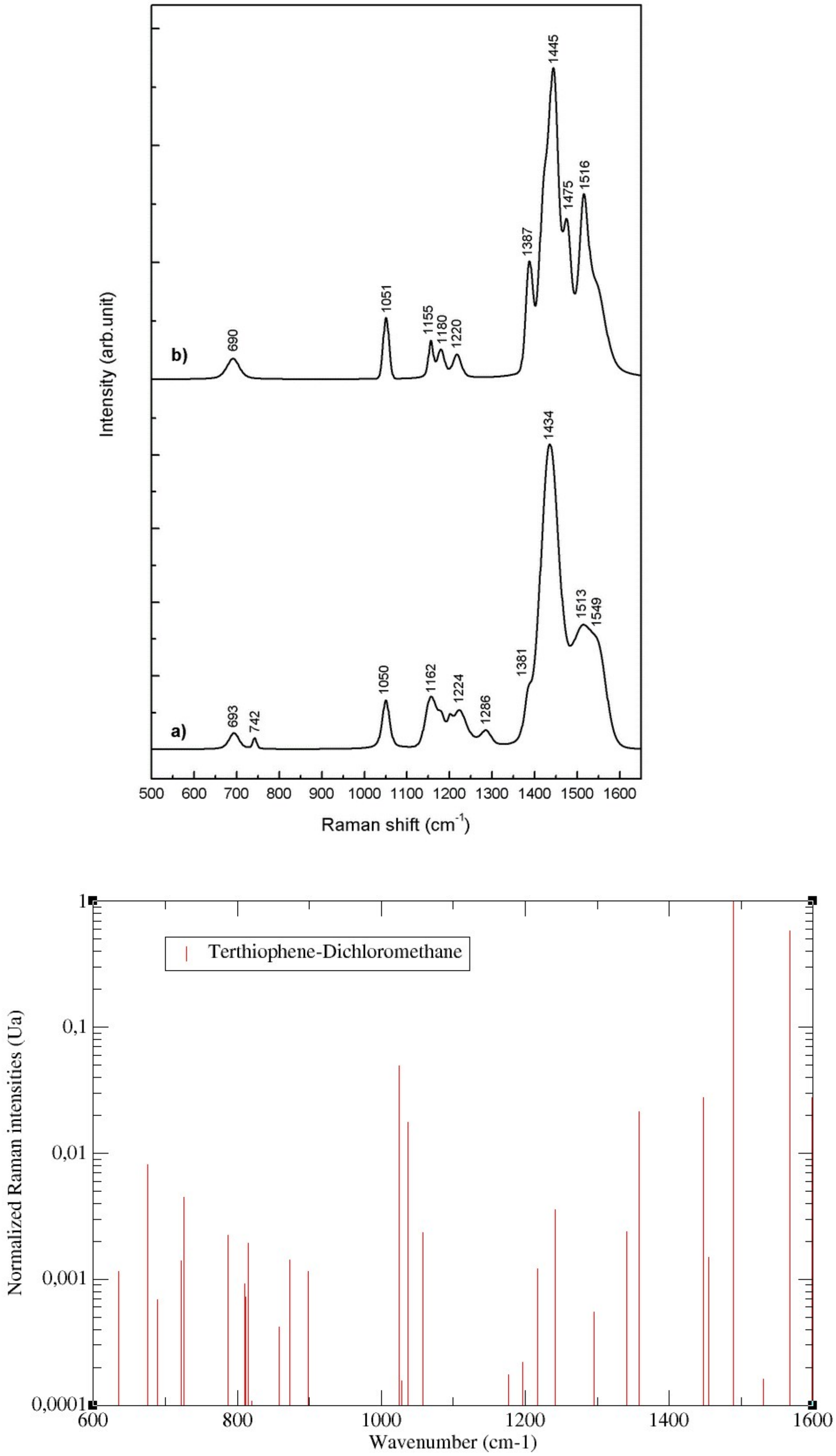
2- Figure S2: SAM (top) in acetonitrile (a), dichloromethane (b) and calculated at M062X/6-31(d,p) theory level (down) $\mathbf{T_2}$ Raman spectra.





For each theoretical spectra (figure S2,S3, S5-S8), the maximum intensity value has been used to normalize the theoretical spectra

3- Figure S3: SAM (top) in acetonitrile (a), in dichloromethane (b) and calculated at M062X/6-31(d,p) theory level (down) **T$_3$** Raman spectra.



4- Table S1: Experimental (in dichloromethane, in acetonitrile) and theoretical vibrational mode for **T_2-Id**.

Experimental Raman Shift (cm^{-1})	scaled theoretical Raman Frequencies calculated in CH_2Cl_2 (cm^{-1})	Vibrational description
643	647	In benzene and pentanedione **C** wagging mode
660-666	650 +673	**ν C-S** with Sulfur and carbon movement + **δ C-S + δ C-C** in benzene and pentanedione **δ C=C** in benzene
682-682	697	**ν C-S** with Sulfur and carbon movement + breathing mode in pentanedione + **δ C=C** and **C-C** in benzene
726-727	716 + 722	**ν C-S** with Sulfur and carbon movement
	719	**H** wagging in benzene
749-747	747	**ν C-S** with Sulfur and carbon movement + **δ C-C** and **C=C** in benzene
770-767	750 - 960	For the majority of vibrational modes: Twisting or Wagging for **C** and **H** in the molecule
	962	**ν C-C and C-S** in thiophene + **ν C-Br + δ H-C**, **C=C** and **C-C** in thiophenes
	971	**Benzene breathing mode + ν C-C** in pentanedione + **ν C-S** in thiophenes **δ H-C, C=C** and **C-C** in thiophenes
	989	**Twisting** in benzene
	1035+1046	**ν C-C** in thiophene and in pentanedione + **ν C-Br** + **δ H-C** in thiophenes
1062-1054	1061	**δ C=C**, **C-C**, **H-C** in benzene + **ν C-C** in pentanedione
1102-1100	1081	**δ H-C** in Benzene, 2 and between thiophene and pentanedione + **ν C-C** in pentanedione and 2
	1121	**δ H-C** in benzene
1158-1155	1144 + 1156	**ν C-C** in pentanedione and in 2 + **δ H-C**, **C-C** and **C=C** in benzene + **δ C=C** and **C-C** between thiophene and pentanedione.
1181-1183	1186	In thiophenes: **ν C=C** and **C-S** + **δ H-C** and **C=C + δ C-Br**
1201-1217	1209 +1237	Inter-ring **ν C-C** and between thiophenes and in pentanedione + **ν C-S** + **δ H-C** in all the molecule + **δ C-C** , **C-S** and **C=C** in thiophenes. + benzene breathing mode
1227-1228	1215	Inter-ring **ν C-C** between thiophenes and in pentanedione + **ν C-S** + **δ H-C** in all the molecule + **δ C-C** and **C=C** in thiophenes.
	1264	**δ C-C** , **C=C**, **H-C** in Benzene + **ν C-C** in pentanedione
1293	1301	**ν C-S** + **ν C-C** in thiophenes and between thiophene and pentanedione + **δ** for **H-C**, **C-C** , **C-S** and **C=C** in thiophene and between thiophene and pentanedione + **δ C-Br**
1327-1325	1337	**ν C=C** in benzene + **ν C-C** in pentanedione and benzene+ **δ H-C** in benzene
1350-1349	1359	**δ C=C**, **C-C** and **H-C** between thiophene and pentanedione + **ν C-C** in pentanedione
1381-1388	1361	In thiophenes: **ν C-C** and **C-S** + **δ C=C**, **C-C** , **C-S and H-C** + inter ring **δ C-C**
1431-1430	1440 + 1451	**ν C=C**, **C-C** and **C-C** inter-ring in thiophenes + **δ C=C, C-C** and **C-S** in thiophenes + **δ H-C** in all the molecule + **δ C-Br**
1471-1474	1459	**ν C=C** in thiophenes and Benzene + **ν C-C** in all the molecule + **δ C=C** and **C-C** in benzene + **δ H-C** in benzene and thiophenes **δ C-S** in thiophenes
	1461	**ν C=C** in benzene + **ν C-C** in pentanedione and benzene + **δ H-C**, **C-C** and **C=C** in benzene
1516-1516	1532	In thiophenes**: ν C=C** + **δ C=C**, **H-C**, **C-C** and **C-S** + **δ C-Br**
1565-1578-1600-1564-1575-1597	1575	In thiophenes: **ν C=C** + inter ring **ν C-C** and **δ C-C** + **δ H-C**, **C-C** , **C=C** and **C-S** + **δ C-Br**

δ C=C: C=C Bending mode, **δ C-C** : C-C Bending mode, **δ C-S** : C-S Bending mode, **δ H-C:** C-H Bending mode , **δ C-Br:** C-Br Bending mode induced by carbon movement
ν C=C: C=C Stretching mode, **ν C-C** : C-C Stretching mode, **ν C-S** : C-S Stretching mode, **ν H-C:** C-H Stretching mode, **ν C-Br:** C-Br Stretching mode induced by carbon movement
2= The thiophene which is the closest to the electron-withdrawing group.

5- Table S2: Experimental (in dichloromethane, in Acetonitrile) and theoretical vibrational mode for **T$_3$-Id**

Experimental Raman shift (cm^{-1})	Scaled theoretical Raman Frequencies calculated in CH$_2$Cl$_2$ (cm^{-1})	Vibrational description
	647	In benzene and pentanedione **C** wagging mode
669-686- 669-685	632 + 664 + 678	**ν C-S** with Sulfur and carbon movement + **δ C-S** + **δ C-C** in benzene and pentanedione + **δ C=C** in benzene.
695-693	697	**ν C-S** with sulfur and carbon movement + breathing mode in pentanedione + **δ C=C** and **C-C** in benzene
	713 + 719 +721	**ν C-S** with Sulfur and carbon movement
729	717	**H** wagging in benzene
750-749	747	**ν C-S** with Sulfur and carbon movement + **δ C=C** and **C-C** in benzene
	750- 960	Twisting or Wagging for **C** and **H** in the molecule.
	970	**Benzene breathing mode** + **ν C-C** in pentanedione + **ν C-S** in thiophenes **δ H-C, C=C** and **C-C** in thiophenes
	988	**Twisting** in benzene
1057-1054	1030 + 1045 + 1036	**ν C-C** in thiophene and pentanedione + **δ H-C** in thiophenes. + **ν C-Br**
	1062	**δ C=C**, **C-C** , **H-C** in benzene + **ν C-C** in pentanedione
1099-1100	1082	**δ H-C** in Benzene, 3 and between thiophene and pentanedione + **ν C-C** in pentanedione and 3
	1121	**δ H-C** in benzene
1157-1157	1144 + 1157	**ν C-C** in pentanedione and in 3 + **δ H-C**, **C-C** and **C=C** in benzene + **δ C=C** and **C-C** between thiophene and pentanedione
	1178	In thiophenes: **ν C=C** and **C-S** + **δ H-C and C-C**
1192-1193	1189	In thiophenes: **ν C=C** and **C-S** + **δ H-C and C-C** + Inter-ring **δ C-C**
1225-1222	1210 + 1223	Inter-ring **ν C-C** between thiophenes and in pentanedione + **ν C-S** + **δ H-C** in all the molecule + **δ C-C** , **C-S** and **C=C** in thiophenes. + benzene breathing mode + **δ C-Br**
	1212	In thiophenes: **ν C=C** and **C-S** + **δ H-C and C-C** + Inter-ring **δ C-C and ν C-C**
	1243	Inter-ring **ν C-C** between thiophenes and in pentanedione + **ν C-S** + **δ H-C** in all the molecule + **δ C-C** and **C=C** in thiophenes.
	1264	**δ C-C** , **C=C**, **H-C** in Benzene + **ν C-C** in pentanedione.
1329-1327	1286 + 1326	**ν C-S** + **ν C-C** in thiophenes and between thiophene and pentanedione + **δ** for **H-C**, **C-C** , **C-S**, **C=C and** in thiophene and between thiophene and pentanedione + **δ C-Br**
1350-1351	1339	**ν C=C** in benzene + **ν C-C** in pentanedione and benzene + **δ H-C** in benzene
	1359	**δ C=C**, **C-C** and **H-C** between thiophene pentanedione + **ν C-C** in pentanedione
1384-1384	1366	In thiophenes: **ν C-C** and **C-S** + **δ C=C**, **C-C** , **C-S** and **H-C** inter ring **δ C-C**
1435-1430-1451*	1437	**ν C=C**, **C-C** and **C-C** inter-ring in thiophenes + **δ C=C, C-S and C-C** in thiophenes + **δ H-C** in all the molecule
1470-1471-1482*	1451+ 1474	**ν C=C**, **C-C** and **C-C** inter-ring in thiophenes + **δ C=C, C-S and C-C** in thiophenes + **δ H-C** in all the molecule + **δ C-Br**
	1458	**ν C=C** in thiophenes and Benzene + **ν C-C** in benzene and in pentanedione + **δ C=C**, **C-C** and **H-C** in benzene
	1462	**ν C=C** in benzene + **ν C-C** in pentanedione and benzene + **δ H-C**, **C-C** and **C=C** in benzene.
1500-1513-1501	1528	In thiophenes**:** **ν C=C** + **δ C=C** , **C-C** , **C-S** and **H-C** + **δ C-Br**
1574-1599-1567-1576-1599*	1558 +1590	In thiophenes: **ν C=C** + inter ring **ν C-C** and **δ C-C** + **δ H-C**, **C-C** , **C=C** and **C-S** + **δ C-Br**

δ C=C: C=C Bending mode, **δ C-C** **:** C-C Bending mode, **δ C-S**: C-S Bending mode, **δ H-C:** C-H Bending mode , **ν C-Br:** C-Br Stretching mode induced by carbon movement
ν C=C: C=C Stretching mode, **ν C-C** **:** C-C Stretching mode, **ν C-S**: C-S Stretching mode, **ν H-C:** c-h Stretching mode, **δ C-Br** **:** C-Br Bending mode induced by carbon movement
3= The thiophene which is the closest to the electron-withdrawing group.
*: Splitted band

6- Table S3: Experimental (in dichloromethane, in acetonitrile) and theoretical vibrational mode for **T$_2$**.

Experimental Raman Shift (cm^{-1})	Scaled theoretical Raman Frequencies calculated in CH$_2$Cl$_2$ (cm^{-1})	Vibrational description
680	660	**ν C-S** with Sulfur and carbon movement + **δ C-S**
701-700	698+699	**H-C** twisting
718	724 + 725	**ν C-S** with Sulfur and carbon movement
751	750 - 960	For the majority of vibrational modes: Twisting or Wagging for **C** and **H** in the molecule.
	1030 + 1033	**ν C-C** + **δ H-C**
1058	1058+1059	**ν C-C** + **δ H-C** + **ν C=C** for C=C away from the bridge between thiophenes
1155-1154	1191	**ν C=C** for C=C close to the bridge between thiophenes + **ν C-S** + **δ H-C**
1207-1224	1207	Inter-ring **ν C-C** and **δ C-C** in the rest of molecule + **ν C-S** + **δ H-C** + **δ C-C** + **δ C=C**
1315	1227	Inter-ring **ν C-C** in the rest of molecule + **ν C-S** + **δ H-C** + **δ C-C** + **δ C=C**
1356	1316	**ν C-S** + **ν C-C** + **δ H-C** + **δ C-C** + **δ C=C**
1389-1388	1353	**ν C-C** and **C-S** + **δ C=C**, **C-C** and **H-C** + inter ring **δ C-C**
1422-1410	1436	**ν C=C** + **C-C** + **δ C=C, C-C**, **H-C** and **C-S** + inter ring **δ C-C** and **ν C-C**
1472	1465	**ν C=C** + **C-C** + **δ C=C, C-C**, **H-C** and **C-S** + inter ring **δ C-C**
1534-1507	1531	**ν C=C** + **β C=C**, **C-C**, **C-S** and **H-C**.
1552	1581	**ν C=C** + inter ring **ν C-C** **and δ C-C** + **β H-C**, **C-C** and **C=C**.

δ C=C: C=C Bending mode, **δ C-C** : C-C Bending mode, **δ C-S**: C-S Bending mode, **δ H-C:** C-H Bending mode
ν C=C: C=C Stretching mode, **ν C-C** : C-C Stretching mode, **ν C-S**: C-S Stretching mode, **ν H-C:** C-H Stretching mode

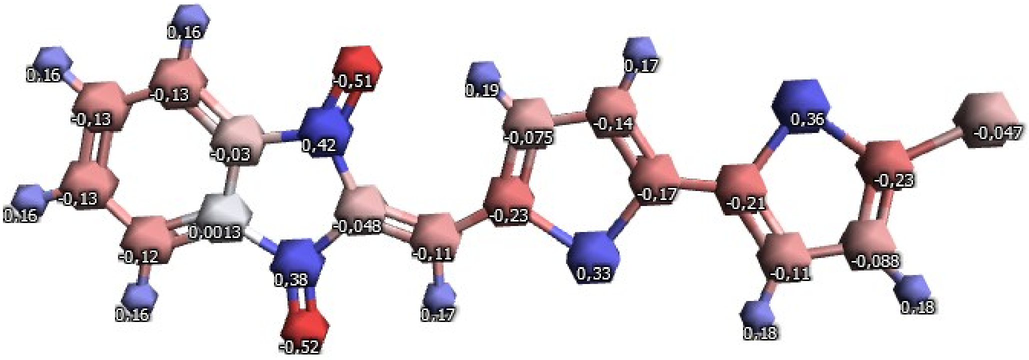
7- Table S4: Experimental (in dichloromethane, in acetonitrile) and theoretical vibrational mode for $\mathbf{T_3}$.

Experimental Raman Shift (cm^{-1})	Scaled theoretical Raman Frequencies calculated in CH_2Cl_2(cm^{-1})	Vibrational description
	634 + 675	**ν C-S** with Sulfur and carbon movement + **δ C-S**
	688 + 689	**H-C** twisting
	722 + 725 + 725	**ν C-S** with Sulfur and carbon movement
	750 - 960	For the majority of vibrational modes: Twisting or Wagging for **C** and **H** in the molecule.
	1025 + 1029 + 1036	**ν C-C + δ H-C**
1051-1050	1057+ 1057	**ν C-C + δ H-C + ν C=C** for C=C away from the bridge between thiophenes
1155-1180-1162	1177 + 1202	**ν C=C** for C=C close to the bridge between thiophenes + **ν C-S** + **δ H-C**
1220-1215	1217	Inter-ring **ν C-C** and **δ C-C** in the rest of molecule + **ν C-S + δ H-C + δ C-C + δ C=C**
	1241	Inter-ring **δ C-C** in the rest of molecule + **ν C-S** + **δ H-C + δ C-C + δ C=C**
	1217	Inter-ring **δ C-C** in the rest of molecule + **ν C-S** + **δ H-C + δ C-C + δ C=C**
	1295	**ν C-S** + **γ C-C + δ H-C + δ C-C + δ C=C**
1387	1340 + 1358	**ν C-C** and **C-S** + **δ C=C**, **C-C** and **H-C** + inter ring **δ C-C**
1421-1475-1475	1454 + 1488	**ν C=C** + **C-C + δ C=C, C-C , H-C** and **C-S** + inter ring **δ C-C** and **ν C-C**
1445-1434	1447	**ν C=C** + **C-C + δ C=C, C-C , H-C** and **C-S** + inter ring **δ C-C**
1516-1513	1530	**ν C=C** + **δ C=C** , **C-C , C-S** and **H-C**.
1553-1549	1568 + 1598	**ν C=C** + inter ring **ν C-C and δ C-C + δ H-C**, **C-C** and **C=C**.

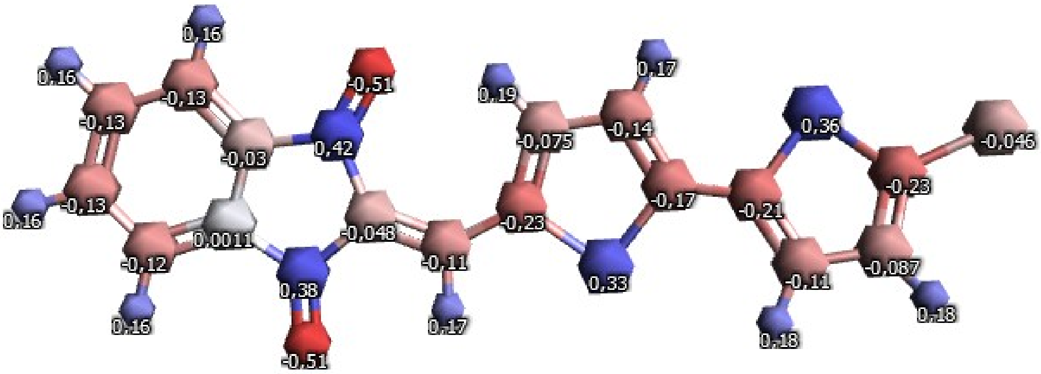
δ C=C: C=C Bending mode, **δ C-C :** C-C Bending mode, **δ C-S**: C-S Bending mode, **δ H-C:** C-H Bending mode
γ c=c: c=c Stretching mode, **γ C-C :** C-C Stretching mode, **γ C-S**: C-S Stretching mode, **γ H-C:** C-H Stretching mode

8- Figure S4: **1** Mulliken atomic charge in acetonitrile (a) and CH_2Cl_2 (b) (M062X/6-31(d,p))

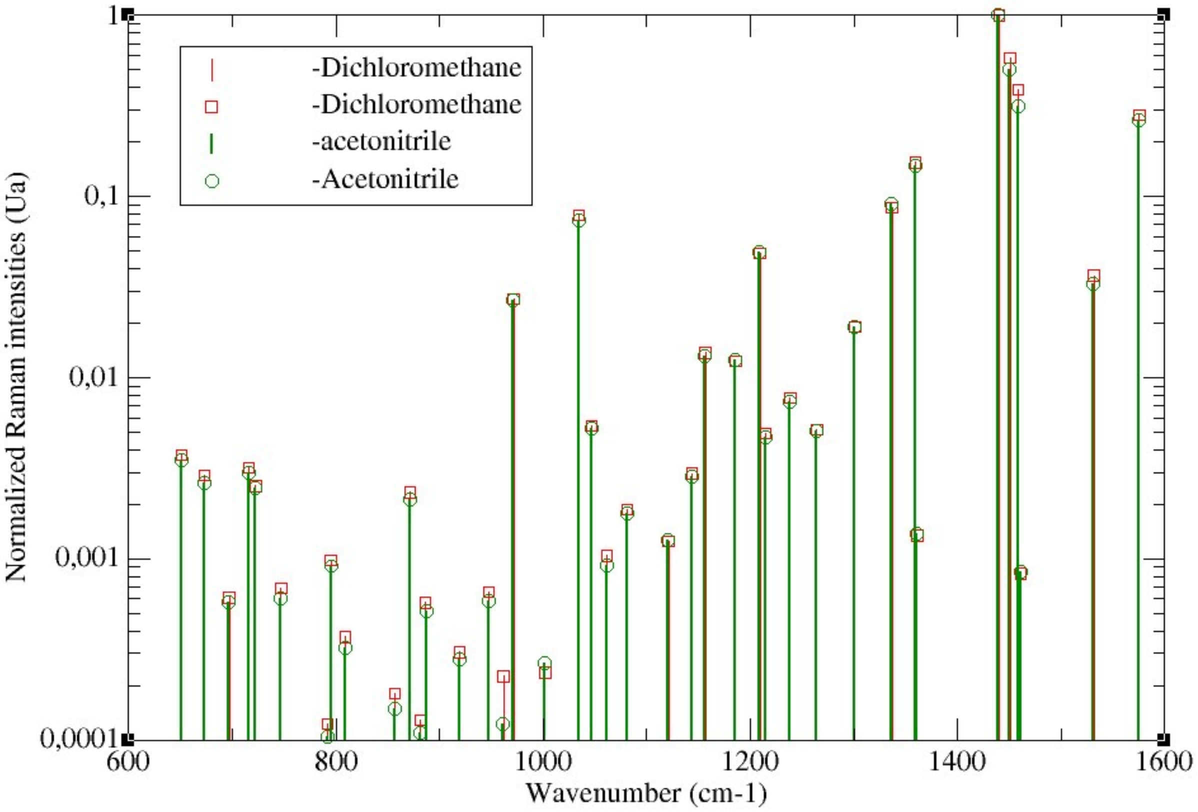
a)



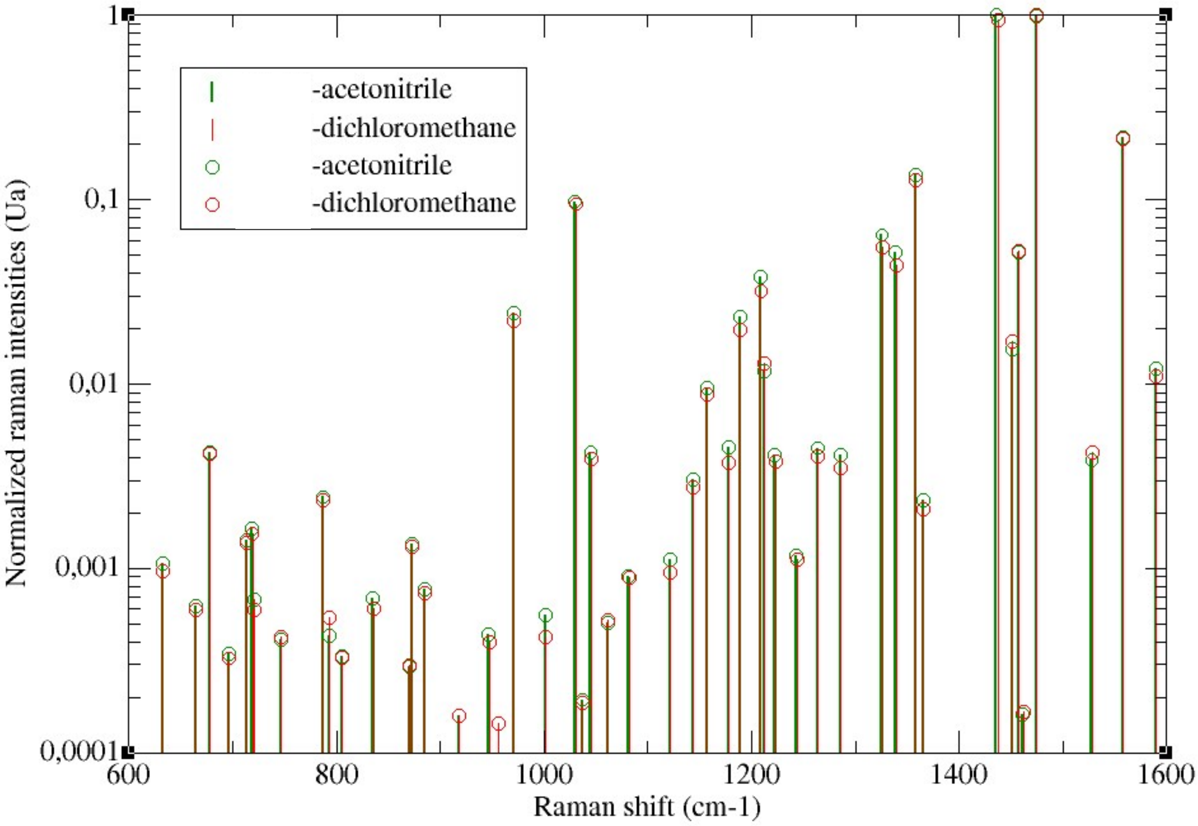
b)



9- Figure S5: Theoretical solvent effect for **T_2-Id** (M062X/6-31(d,p))

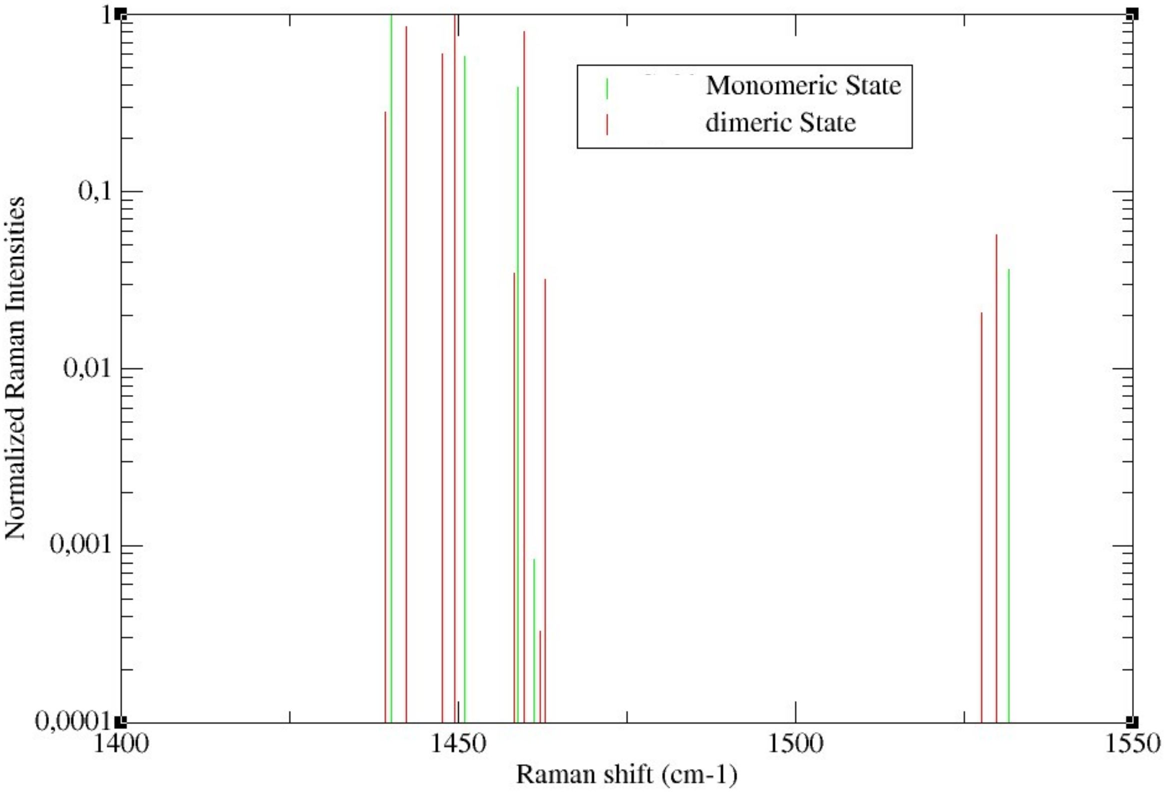


10- Figure S6: Theoretical solvent effect for **2** (M062X/6-31(d,p))



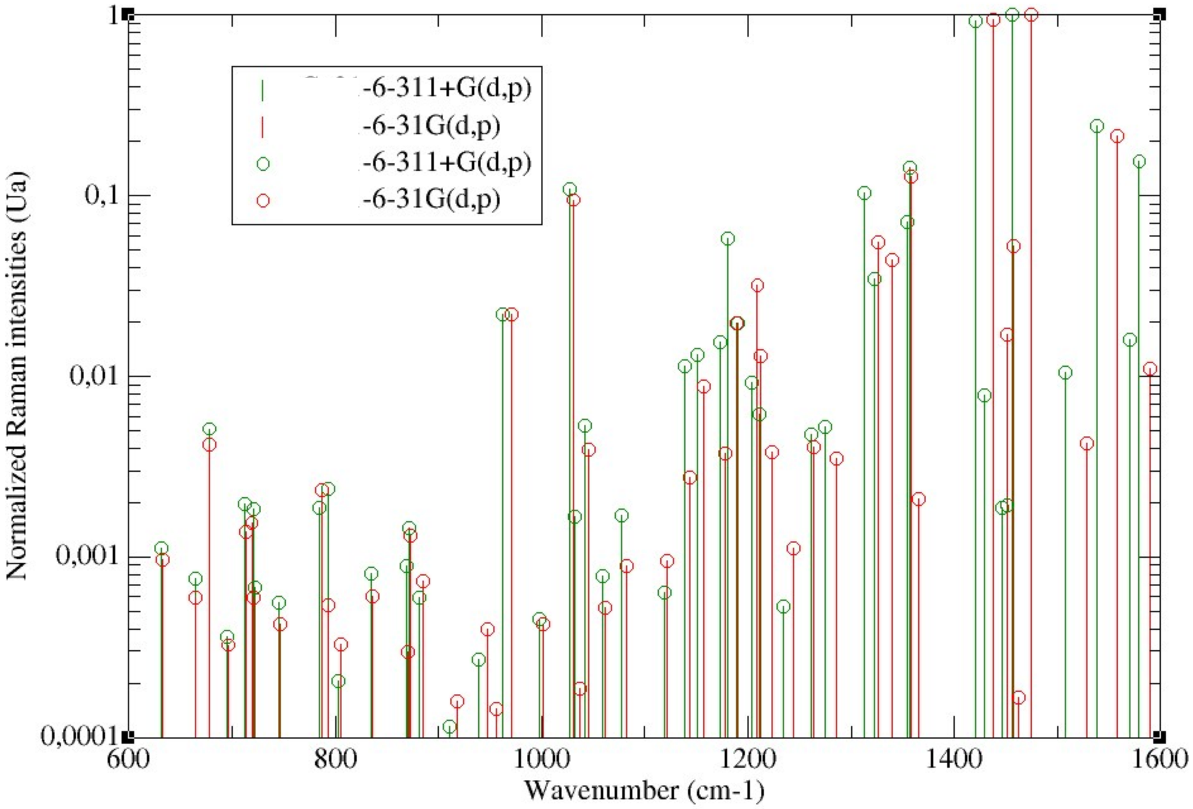
The only observed difference is for the maximal intensities. Indeed, in CH_2Cl_2 this intensity is obtained at 1437 cm^{-1} whereas it is at 1474 cm^{-1} for Acetonitrile calculation.

11- Figure S7: **1**, Raman theoretical comparison between monomeric and dimeric-parallel state.



Vibrational mode distribution is the same for monomers and dimers. Dimerization induces vibrational modes duplication**.** These results are the same for Cp21, bithiophene and terthiophene in all spectra regions when a comparison between monomeric and dimeric-parallel or monomeric and dimeric-antiparallel state is performed.

12- Figure S8: Basis set effect for **2**.

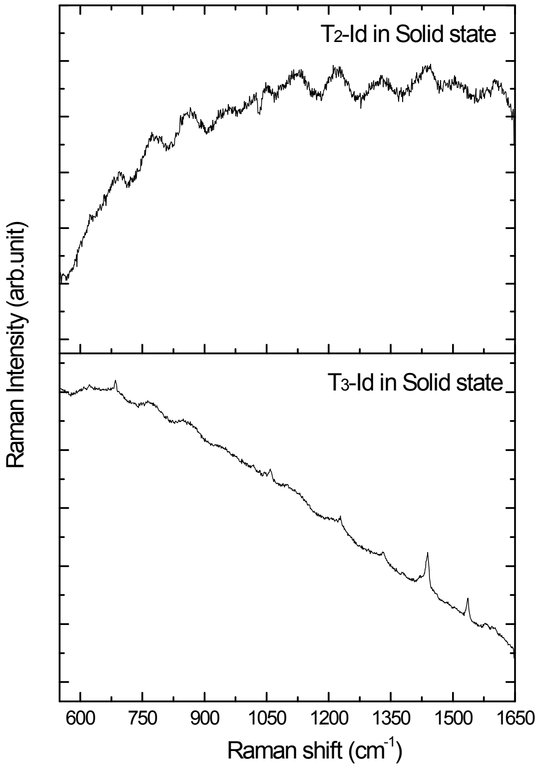


As we can see in Figure S9 the only differences between the calculations for Cp21 in Dichloromethane with 6-311+(d,p) basis set and 6-31(d,p) basis set are in the 1400-1600 spectra area. Indeed, as we can see in table S1 some vibrational modes are shifted. For example, the Vibrational mode at 1437 cm^{-1} for 6-31(d,p) basis set calculation is the same as the one at 1420 cm^{-1} for 6-311+(d,p) basis set calculation.

13- Table S5: vibrational modes shift between **T_3-Id** 6-31(d,p) and **T_3-Id** 6-311+(d,p) basis set in 1430 -1600 cm^{-1} spectra area for **2**.

2 6-31(d,p)	**2** 6-311+(d,p)
1437 ◄	► 1420
1451 ◄	► 1429
1457 ◄	► 1447
1461 ◄	► 1452
1475 ◄	► 1455
1527 ◄	► 1508
1557 ◄	► 1538
1590 ◄	► 1571
1602 ◄	► 1579

14- Figure S9: **T_3-Id** and **T_2-Id** Raman spectra in solid state



15- Figure S10: **T_3-Id** and **T_2-Id** Raman spectra measured in various areas of the drop