Photophysical properties of poly(3,4-ethylenedioxythiophene)/permethylated β- and γ- cyclodextrin polyrotaxanes

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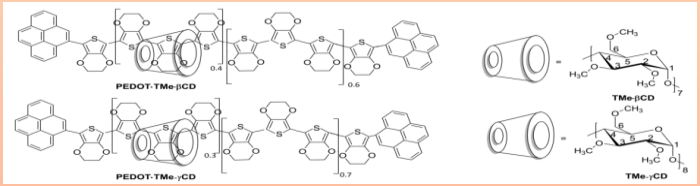

Figure 1. The chemical structures of the investigated compounds.

Poly(3,4-ethylenedioxythiophene) (PEDOT) is known as an interesting material for optoelectronic applications. Since the solubility of PEDOT compound is a critical element for the application, a lot of synthetic procedures such as the encapsulation of PEDOT backbone into the macrocyclic cavities via noncovalent interactions have been applied.

Herein, we continue to provide extensive insights into the excited state dynamics of absorption and emission (fluorescence and phosphorescence) in water and acetonitrile (ACN) solutions of two PEDOT·TMe-βCD and PEDOT·TMe-γCD polyrotaxanes.

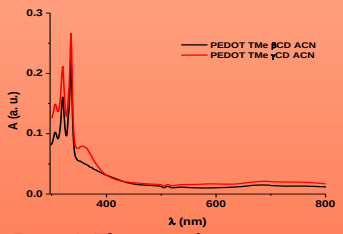

Figure 2. Electronic absorption spectra in **ACN0**

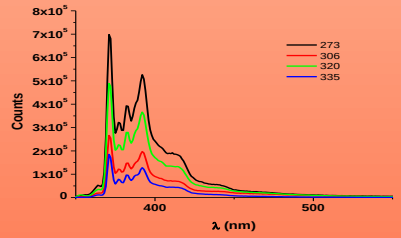

Figure 3. Fluorescence spectra of **PEDOT TMe βCD** in **ACN**

Also, the quantum yields measurements and time resolved fluorescence experiments were performed in both water and ACN in solutions. The quantum yields with absolute values from 0.0005 to 0.76 were found depending on the solvent nature, and lifetimes from 0.4 ns to 29 ns were obtained for fluorescence and phosphorescence lifetime with values in the range 0.8 to 9 μs.

ACKNOWLEDGMENTS

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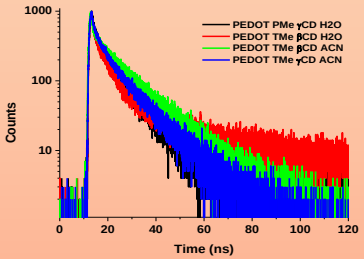

Figure 4. Decays in **$H_2$0** and **ACN** with λ_{ex}=375 nm

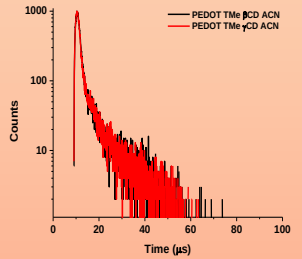

Figure 5. Phosphorescence lifetime in **ACN** with λ_{ex}=355 nm

Table 1.The quantum yields and lifetimes

Sample	Solvent	λ_{ex} (nm)	λ_{em} (nm)	τ_1 (ns)	τ_2 (ns)	τ_3 (ns)	Φ_{FL} (%)	Φ_{Ph} (%)
PEDOT TMe βCD	H_2O	375	403	0.441 (17.50%)	5.057 (49.29%)	28.947 (33.21%)	0.05	-
PEDOT PMe γCD	H_2O	355	675	843 (64.41%)	7635 (35.59%)	-	2.19	0.10
		375	404	1.766 (29.31%)	9.706 (70.69%)	-		
PEDOT TMe γCD	ACN	355	440	1104 (69.20%)	8799 (30.80%)	-	1.89	47.22
		375	390	1.377 (21.88%)	10.492 (78.12%)	-		
PEDOT TMe βCD	ACN	355	440	1134 (69.80%)	8937 (30.20%)	-	2.49	76.17
		375	391	0.583 (13.19%)	12.701 (86.81%)	-		

The transient absorption map revealed ground state bleaching bands (GSB) in the range 270- 315 nm, whereas an absorption band in excited state (ESA) occurs at shorter wavelengths from 210 to 250 nm and more than one excited state ($S_n > 1$). At longer wavelength, from 390 to 455 nm negative bands appeared which can be assigned to the stimulated emissions (SE).