

Supporting Information


Solvent Organization Around the Noncanonical Part of Amino Acid Modulates its Fluorescence Properties

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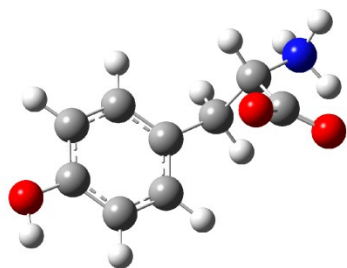
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Table S1: The maxima of emission (nm) of TFTyr in ETH and TFE solvents has been calculated using different methods and solvent models

Method /Solvent Model	Emission of TFTyr in ETH		Emission of TFTyr in ET 	
	Calculated	Experimental	Calculated	Experimental
B3LYP/6-31+g(d) PCM	386	312	386	308
Cam- B3LYP /6-31+g(d,p) PCM	295		295	
Cam- B3LYP /6-31+g(d,p) SMD	295		295	
Cam- B3LYP /6-31+g(d,p) SMD+ dispersion	318		334	
Cam- B3LYP /6-31+g(d,p) IEF-PCM	313		303	

(a) Tyr



(b) TFTyr

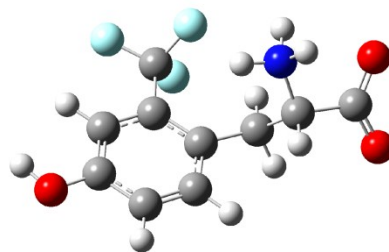


Figure S1: Optimized structure of Tyr and TFTyr monomer in  obtained from the CAM-B3LYP/6-31+G(d,p) level of theory .

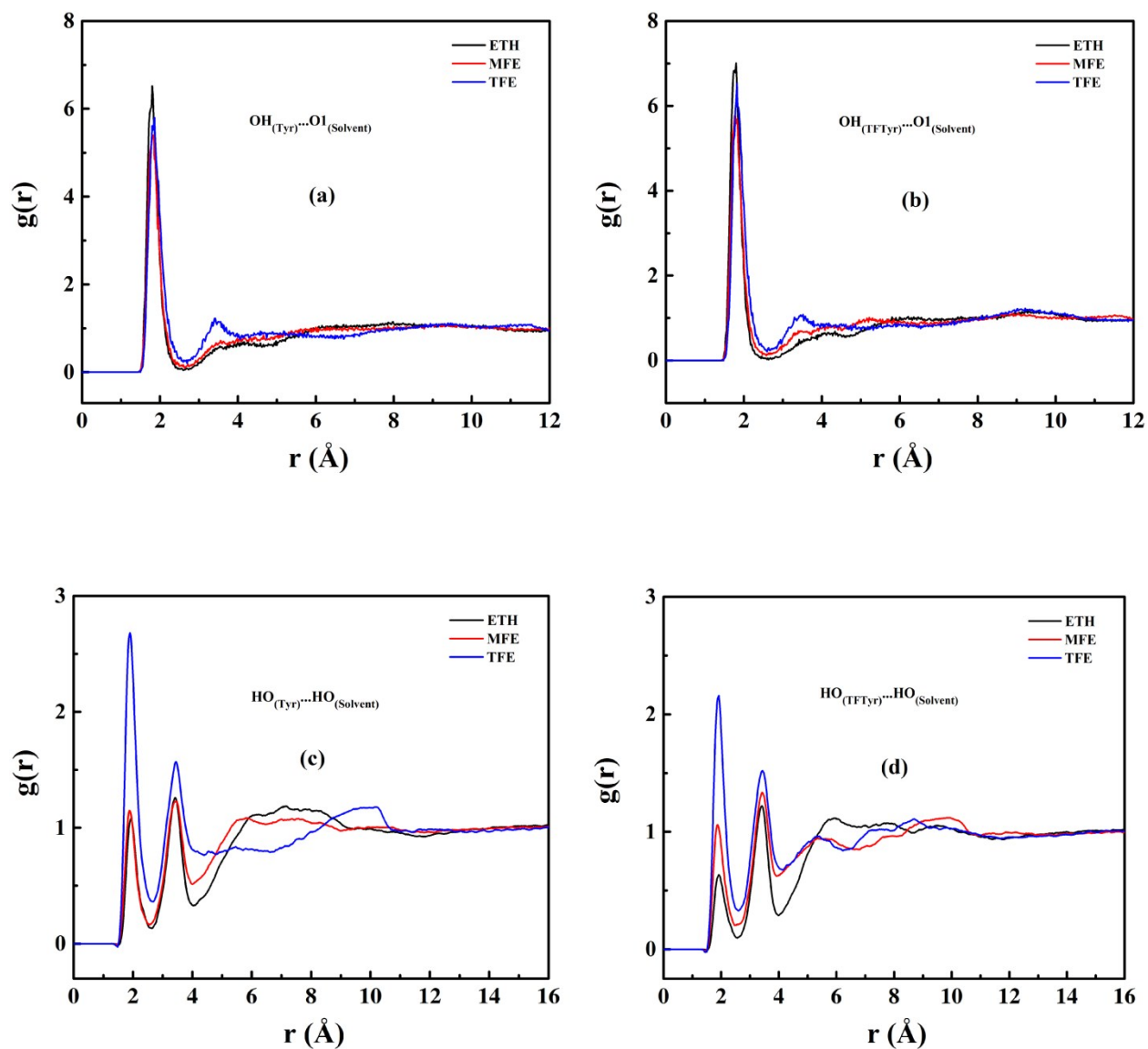


Figure S2: Structural organization of solvent molecules near phenolic OH moiety of Tyr and TFTyr. Radial distribution functions of O1 atom of alcohols from the H atom of phenolic OH of zwitterionic (a) Tyr and (b) TFTyr. Radial distribution function of H atom attached to O1 atom of alcohols from O atom of phenolic OH of zwitterionic (c) Tyr and (d) TFTyr.

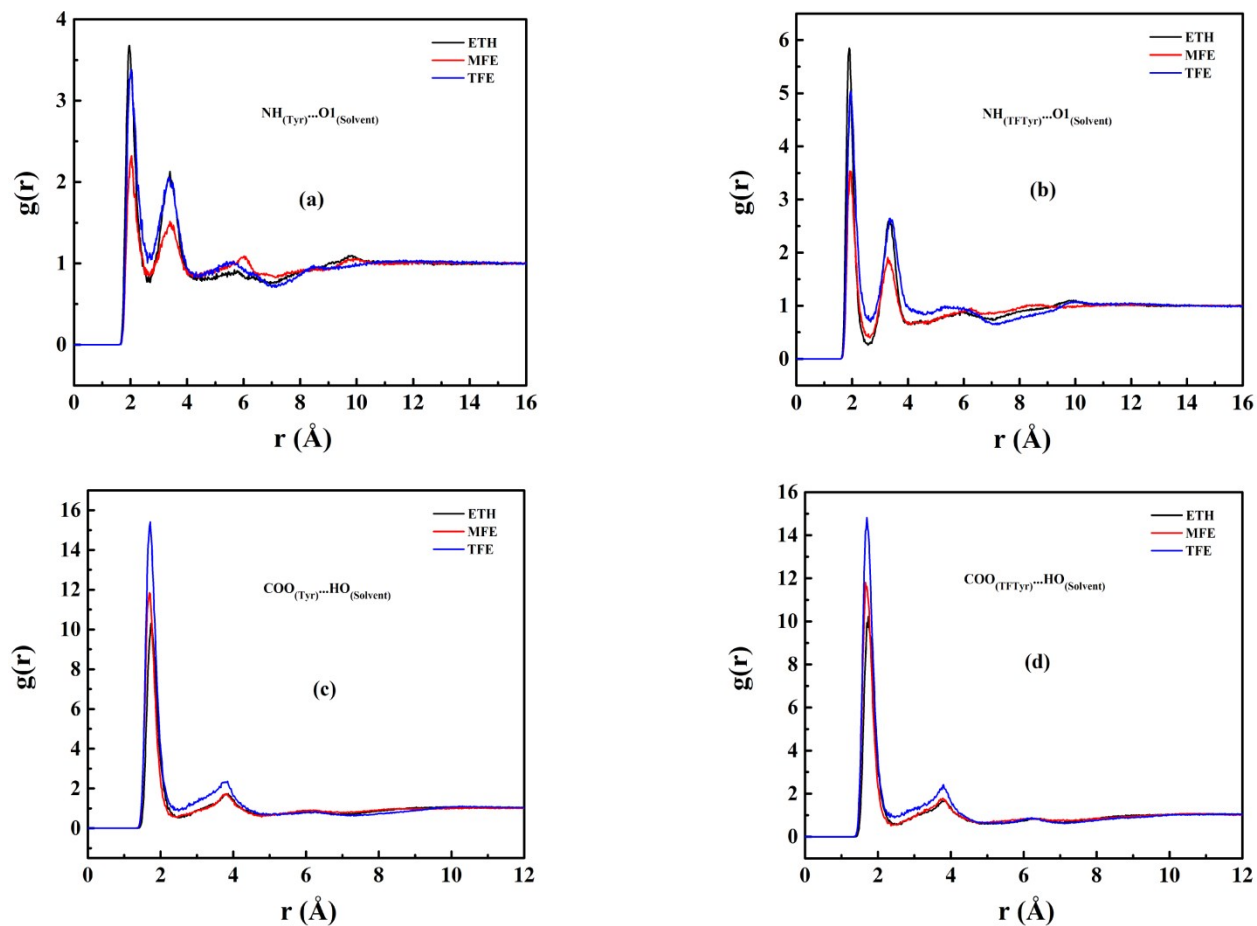


Figure S3: Radial distribution function of O1 atom of alcohols from H atoms of NH_3^+ group of zwitterionic (a) Tyr and (b) TFTyr. Radial distribution function of H atom attached to O1 atom of alcohols from O atoms of CO_2^- moiety of zwitterionic (c) Tyr and (d) TFTyr.

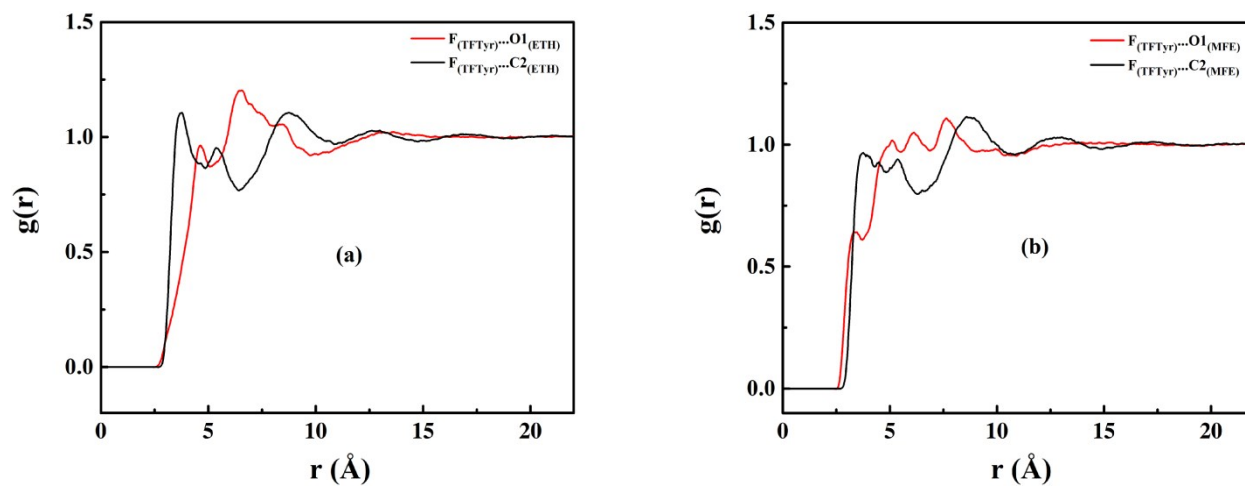


Figure S4: Radial distribution function of O1 atom and C2 atom of alcohols around CF_3 moiety of zwitterionic TFTyr in (a) ETH and (b) MFE, respectively.

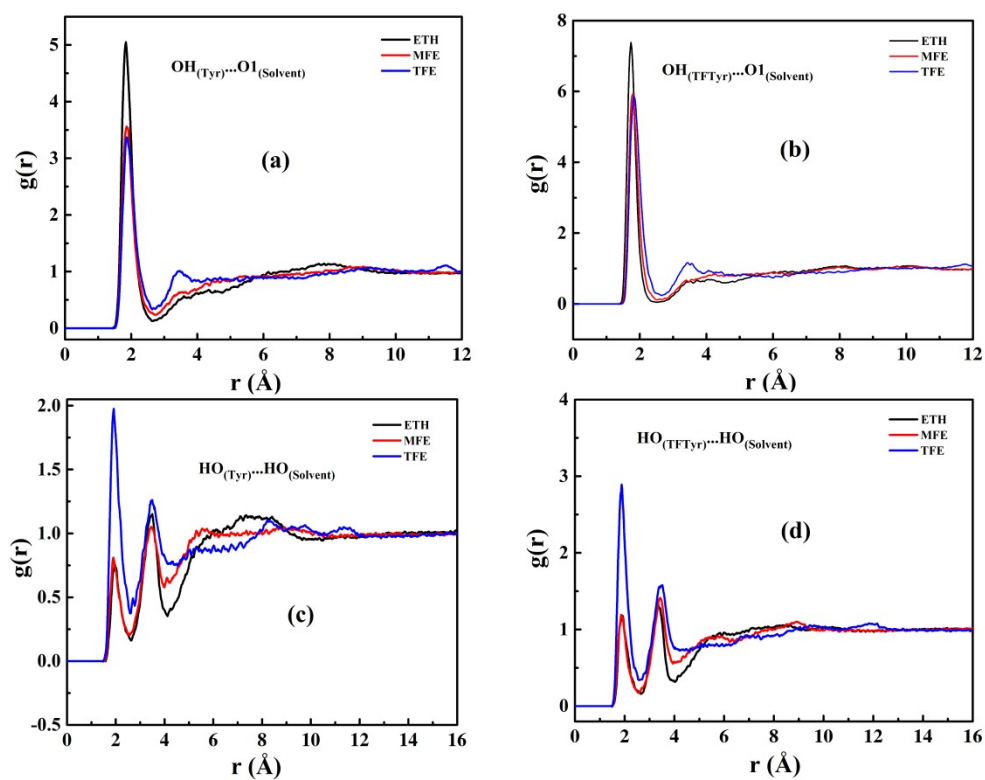


Figure S5: Structural organization of solvent molecules near phenolic OH moiety of Tyr and TFTyr in their neutral form. Radial distribution functions of O1 atom of alcohols from the H atom of phenolic OH of (a) Tyr and (b) TFTyr. Radial distribution function of H atom attached to O1 atom of alcohols from O atom of phenolic OH of (c) Tyr and (d) TFTyr.

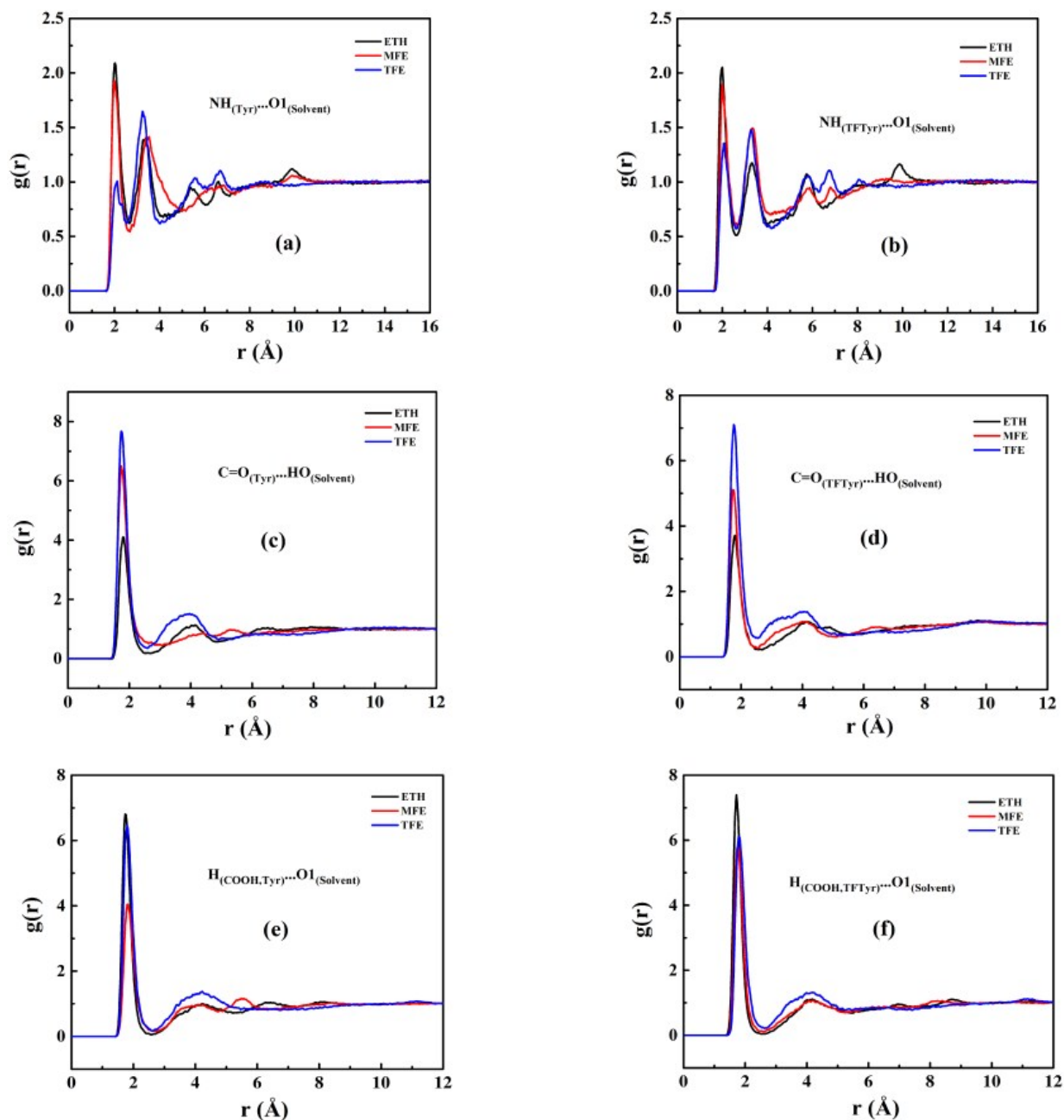


Figure S6: Radial distribution function of O1 atom of alcohols from H atoms of NH_2 group of (a) Tyr and (b) TFTyr in their neutral form. Radial distribution function of H atom attached to O1 atom of alcohols from C=O moiety of neutral (c) Tyr and (d) TFTyr. Radial distribution function of O1 atom of alcohols from H atom attached to COOH moiety of neutral (e) Tyr and (f) TFTyr.

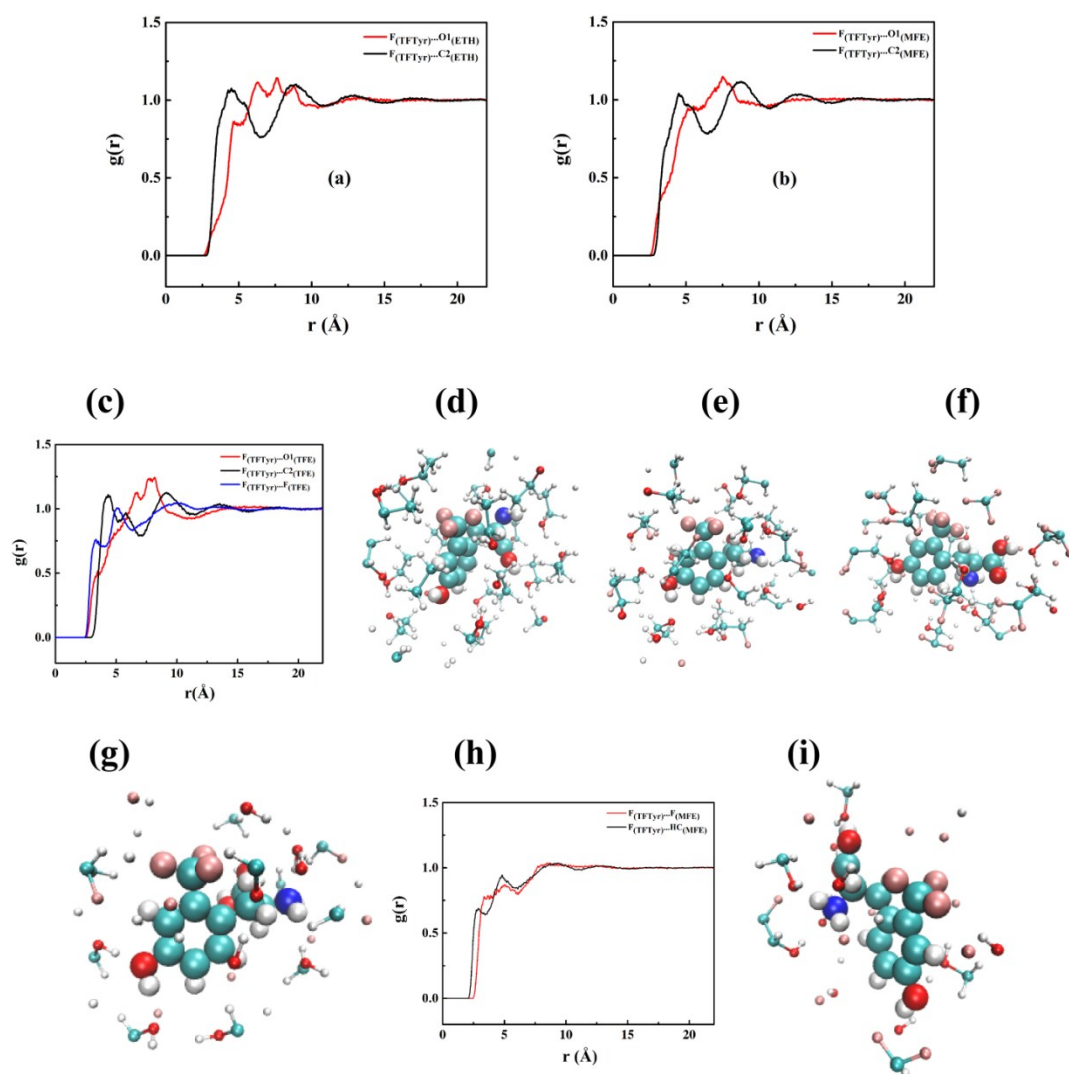


Figure S7: Radial distribution function of O1 atom and C2 atom of alcohols around CF_3 moiety of neutral TFTyr in (a) ETH and (b) MFE, respectively. Solvent organizations around CF_3 moiety of neutral TFTyr. (c) $g(r)$ of O_1 (red) and C_2 (black) atoms of TFE from the CF_3 moiety of TFTyr. Comparatively enhanced first peak value for C_2 atom suggests the preferential solvation by C_2 end of TFE. Similar preferential solvation by other alcohols is also observed. Pictorial representation of the first solvation layer around CF_3 moiety of TFTyr in (d) ETH, (e) MFE, and (f) TFE suggesting the preferential solvation by C_2 end of alcohols in all the cases. Blue line in the $g(r)$ plot (c) shows the possibility of fluororous ($\text{F}\dots\text{F}$) interaction between the CF_3 moiety of TFTyr and TFE solvents. Pictorial representations of the atoms present within 3.5 \AA from the CF_3 moiety of TFTyr in MFE (g) and (h) represents the $g(r)$ of F and H (C_2) atoms of MFE from CF_3 moiety of TFTyr. Shifting of the first peak towards lower distances for H (C_2) atom compared to F atom indicates the possibility of the formation of specific $\text{FCH(MFE)}\dots\text{F}_3\text{C(TFTyr)}$ interactions. The pictorial representations of the atoms present within 3.5 \AA from the CF_3 moiety of TFTyr in TFE are shown in (i) which confirms the presence of ($\text{F}\dots\text{F}$) interaction between the CF_3 moiety of TFTyr and TFE solvents.

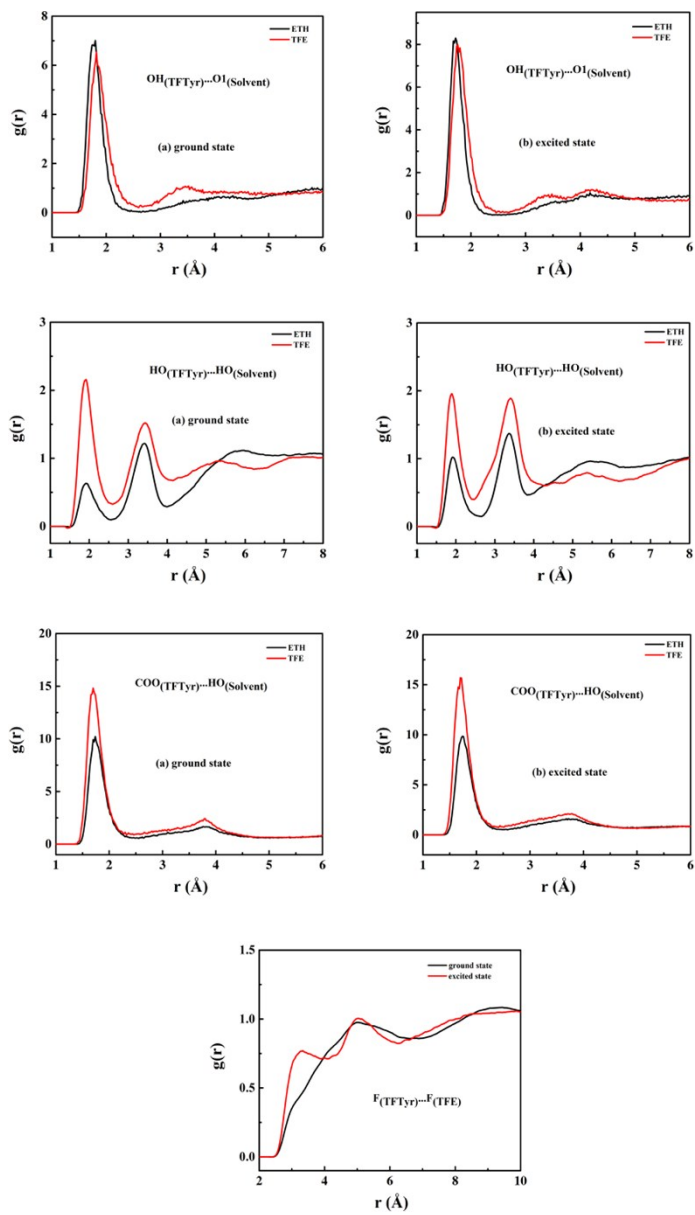
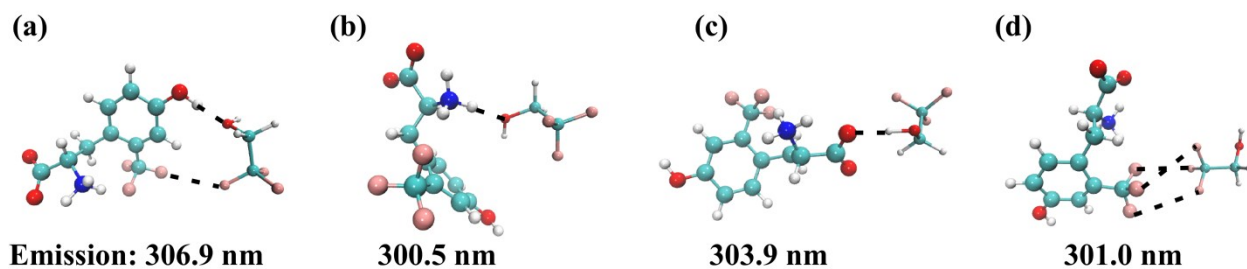


Figure S8: Comparison of the different radial distribution function of zwitterionic TFTyr in ETH and TFE in its (a) ground state and (b) excited state.

TFTyr in TFE 1:1 cluster



TFTyr in TFE 1:2 cluster

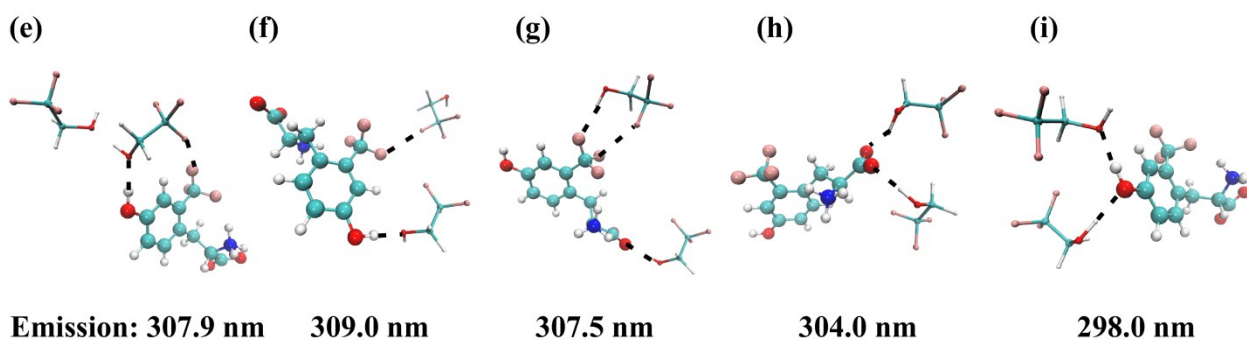


Figure S9: The ground state optimized structures of TFTyr in TFE at its different binding sites. The calculated value of the peak maxima of the emission spectra are given below to the corresponding structure.

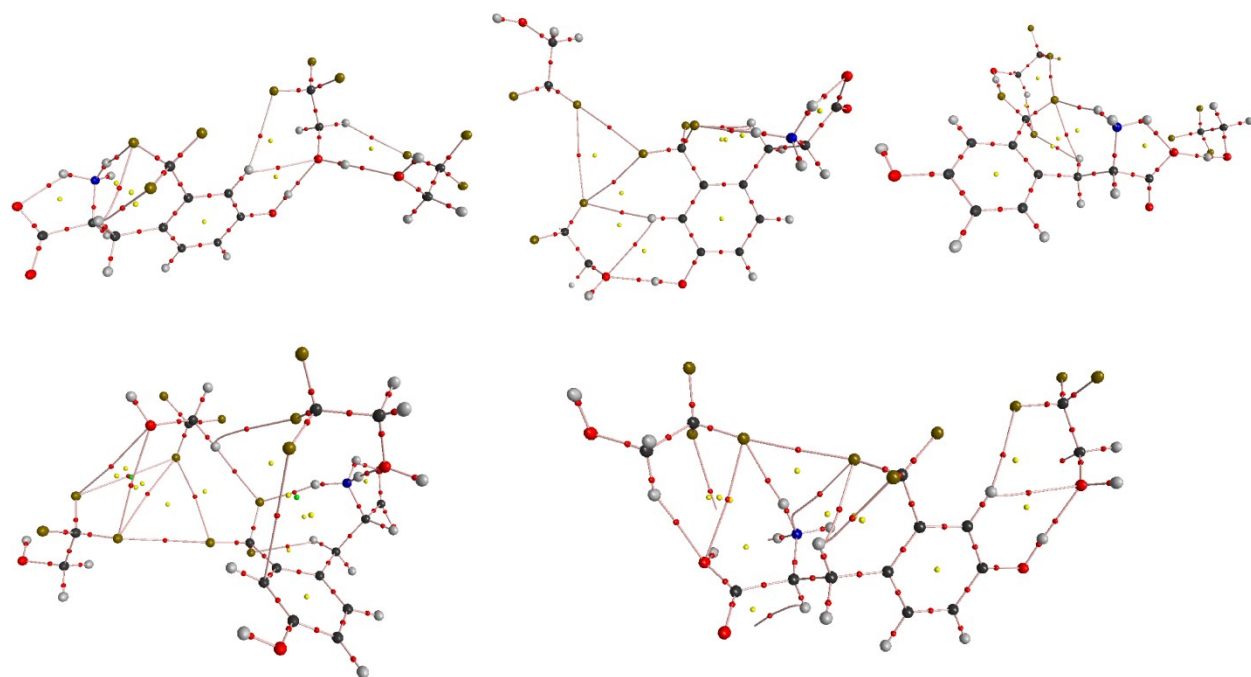


Figure S10: Molecular graph obtained from the AIM calculation of TFTyr in TFE shows the presence of (3,-1) bond critical point at the F...F contacts.

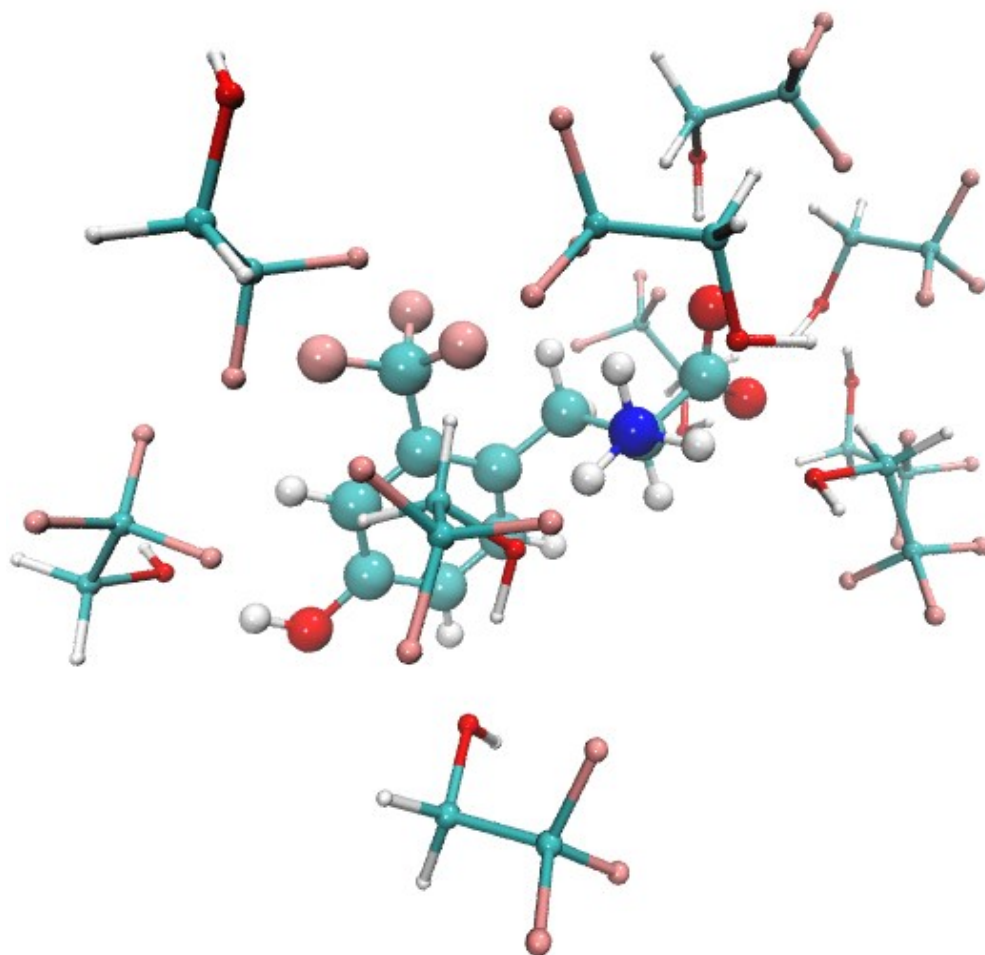


Figure S11: The optimized structure of 1:10 cluster of TFTyr and TFE using the ONIOM method. Here, probe molecule has been treated with the CAM-B3LYP/6-31+G (d,p) method whereas RHF/3-21G (d) method has been implemented on the TFE solvent molecules.

Method of calculation of Quantum Yield (Φ)

It is extremely difficult to measure exact quantum yield because exact photon flux has to be maintained during measurement of the emission spectra. Hence, quantum yield is generally measured with respect to the known standard sample whose quantum yields are already known. In this study, quantum yield has been measured by the standard procedure. We have calculated quantum yield (Φ) of Tyr and TFTyr in alcoholic solvents by using the following equation¹ :

$$\Phi = \Phi_R \times \frac{I}{I_R} \times \frac{A_R}{A} \times \frac{\eta^2}{\eta_R^2}$$

Where Φ_R is the quantum yield of the standard or reference, $A = (1 - 10^{-OD})$ refers to the optical density correction of the emission spectra of the amino acids in different solvents, I is the integrated area under the emission spectra of the solution and η is the refractive index of the solvents taken. The values of refractive index used in this study for ETH, MFE and TFE were 1.361, 1.365 and 1.291 respectively. Subscript R refers to the reference solution. The quantum yield of tyrosine in water has been taken as reference as it has already been reported by several groups^{1,2}. We have measured the absorption spectra of Tyr and TFTyr in ETH and fluorinated ETHs keeping all the instrumental parameters same for each measurements. The emission spectrum of each amino acid has been measured in different solvents using the same excitation as well as other instrumental conditions. The emission spectra were OD corrected to extract OD independent emission integrated area.

References:

1. Chen, R. F., Fluorescence Quantum Yields of Tryptophan and Tyrosine. *Anal. Lett.* **1967**,1 (1), 35-42.
2. Lakowicz, J. R., *Principles of Fluorescence Spectroscopy*. 3rd ed.; Springer USA:**2007**.