Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics

Fluorescence properties of organic dyes: Quantum chemical studies on the green/blue neutral and protonated DMA-DPH emitters in polymer matrices

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Supplementary Information

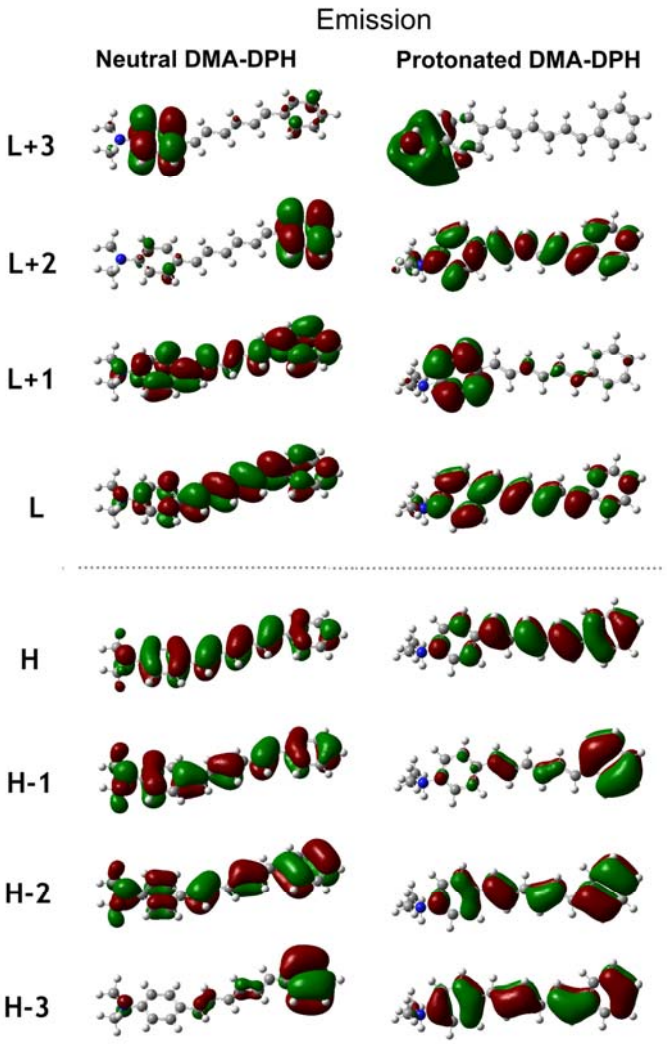

Figure S1 Highest occupied (H, H-1, H-2, H-3) and lowest unoccupied (L, L+1, L+2, L+3) orbitals at the CAM-B3LYP/6-311G(d,p) level for DMA-DPH_n and DMA-DPH_p at their emission geometries..

Table S1. Low-lying absorption energies ΔE(eV), wavelengths λ(nm) and relevant oscillator strengths f for the (S_2,S_3,S_4,S_5) ← S_0 excitations of DMA-DPH_n in gas phase and in various solvents at different levels of theory. See text for description of the methods.

Level	$S_2 \leftarrow S_0$		$S_3 \leftarrow S_0$		$S_4 \leftarrow S_0$		$S_5 \leftarrow S_0$	
	ΔE	λ(f)	ΔE	λ(f)	ΔE	λ(f)	ΔE	λ(f)
Gas phase								
TD-B3LYP/6-311G(d,p)	3.711	334.1(0.28)	3.997	310.2(0.08)	4.114	301.4(0.01)	4.322	286.9(0.00)
TD-B3LYP/TZVPP	3.687	336.3(0.23)	3.917	316.5(0.11)	4.033	307.5(0.02)	4.286	289.3(0.00)
TD-CAM-B3LYP/6-311G(d,p)	4.497	275.7(0.07)	4.696	264.0(0.02)	4.915	252.2(0.04)	5.035	246.2(0.02)
TD-CAM-B3LYP/TZVPP	4.396	282.1(0.08)	4.654	266.4(0.01)	4.844	255.9(0.06)	4.986	248.7(0.02)
RICC2/def2-SVP	4.318	287.1(0.07)	4.596	269.8(0.27)				
RICC2/TZVPP	4.149	298.8(0.08)	4.421	280.4(0.18)				
Benzene								
LR-TD-B3LYP/6-311G(d,p)	3.647	339.9(0.28)	3.941	314.6(0.05)	4.055	305.7(0.04)	4.207	294.7(0.00)
LR-TD-CAM-B3LYP/6-311G(d,p)	4.408	281.3(0.10)	4.545	272.8(0.01)	4.895	253.3(0.05)	4.989	248.5(0.02)
Hexane								
LR-TD-B3LYP/6-311G(d,p)	3.663	338.4(0.27)	3.962	313.0(0.05)	4.075	304.3(0.03)	4.233	292.9(0.00)
LR-TD-CAM-B3LYP/6-311G(d,p)	4.441	279.2(0.09)	4.581	270.6(0.01)	4.903	252.9(0.04)	5.001	247.9(0.02)
Diethylether								
LR-TD-B3LYP/6-311G(d,p)	3.647	340.0(0.31)	3.953	313.6(0.05)	4.056	305.7(0.03)	4.216	294.0(0.00)
LR-TD-CAM-B3LYP/6-311G(d,p)	4.426	280.1(0.10)	4.566	271.5(0.01)	4.898	253.2(0.05)	4.993	248.3(0.02)
Methyl Propanoate								
LR-TD-B3LYP/6-311G(d,p)	3.640	340.6(0.32)	3.948	314.1(0.05)	4.049	306.2(0.04)	4.208	294.6(0.00)
SS-TD-B3LYP/6-311G(d,p)								
LR-TD-B3LYP/TZVPP	3.622	342.3(0.28)	3.862	321.0(0.06)	3.968	312.5(0.05)	4.170	297.4(0.00)
LR-TD-CAM-B3LYP/6-311G(d,p)	4.418	280.6(0.10)	4.556	272.1(0.02)	4.895	253.3(0.05)	4.989	248.5(0.02)
SS-TD-CAM-B3LYP/6-311G(d,p)								
LR-TD-CAM-B3LYP/TZVPP	4.320	287.0(0.10)	4.513	274.8(0.01)	4.821	257.2(0.07)	4.942	250.9(0.02)
Acetone								
LR-TD-B3LYP/6-311G(d,p)	3.632	341.4(0.34)	3.942	314.5(0.05)	4.040	306.9(0.04)	4.200	295.2(0.00)
LR-TD-B3LYP/TZVPP	3.613	343.2(0.30)	3.857	321.5(0.06)	3.958	313.2(0.05)	4.162	297.9(0.00)
LR-TD-CAM-B3LYP/6-311G(d,p)	4.410	281.1(0.10)	4.550	272.5(0.01)	4.892	253.4(0.06)	4.985	248.7(0.02)
LR-TD-CAM-B3LYP/TZVPP	4.312	287.5(0.10)	4.507	275.1(0.01)	4.818	257.3(0.07)	4.938	251.1(0.02)
Acetonitrile								
LR-TD-B3LYP/6-311G(d,p)	3.559	348.3(0.25)	3.841	322.8(0.03)	3.998	310.1(0.09)	4.109	301.8(0.00)
LR-TD-B3LYP/TZVPP	3.547	349.6(0.23)	3.751	330.5(0.03)	3.920	316.3(0.10)	4.057	305.6(0.01)
LR-TD-CAM-B3LYP/6-311G(d,p)	4.250	291.7(0.10)	4.416	280.8(0.04)	4.870	254.6(0.07)	4.955	250.2(0.02)
LR-TD-CAM-B3LYP/TZVPP	4.170	297.3(0.12)	4.345	285.3(0.03)	4.796	258.5(0.08)	4.906	252.8(0.02)

Table S2. Low-lying absorption energies ΔE(eV), wavelengths λ(nm) and relevant oscillator strengths f for the (S_2,S_3,S_4,S_5) ← S_0 excitations of DMA-DPH_p in gas phase and in various solvents at different levels of theory. See text for description of the methods.

Level	$S_2 \leftarrow S_0$		$S_3 \leftarrow S_0$		$S_4 \leftarrow S_0$		$S_5 \leftarrow S_0$	
	ΔE	λ(f)	ΔE	λ(f)	ΔE	λ(f)	ΔE	λ(f)
Gas phase								
TD-B3LYP/6-311G(d,p)	3.181	389.8(0.12)	3.518	352.4(0.01)	3.548	349.4(0.00)	3.814	325.1(0.45)
TD-B3LYP/TZVPP	3.128	396.4(0.16)	3.493	354.9(0.00)	3.533	350.9(0.01)	3.803	326.1(0.44)
TD-CAM-B3LYP/6-311G(d,p)	4.157	298.2(0.07)	4.650	266.6(0.01)	4.756	260.7(0.02)	4.880	254.1(0.23)
TD-CAM-B3LYP/TZVPP	4.075	304.3(0.09)	4.640	267.2(0.02)	4.708	263.3(0.03)	4.864	254.9(0.19)
RICC2/def2-SVP	4.114	301.3(0.06)	4.478	276.8(0.01)				
RICC2/TZVPP	3.871	320.3(0.10)	4.369	283.8(0.02)				
Benzene								
LR-TD-B3LYP/6-311G(d,p)	3.561	348.2(0.08)	3.884	319.2(0.16)	3.915	316.7(0.08)	4.280	289.7(0.00)
LR-TD-CAM-B3LYP/6-311G(d,p)	4.518	274.4(0.06)	4.770	259.9(0.00)	4.872	254.5(0.01)	5.051	245.5(0.10)
Hexane								
LR-TD-B3LYP/6-311G(d,p)	3.486	355.7(0.08)	3.828	323.8(0.04)	3.888	318.8(0.26)	4.272	290.2(0.01)
LR-TD-CAM-B3LYP/6-311G(d,p)	4.460	278.0(0.06)	4.767	260.1(0.01)	4.843	256.0(0.01)	5.026	246.7(0.12)
Diethylether								
LR-TD-B3LYP/6-311G(d,p)	3.743	331.3(0.09)	3.929	315.6(0.11)	4.063	305.2(0.01)	4.289	289.1(0.00)
LR-TD-CAM-B3LYP/6-311G(d,p)	4.615	268.7(0.04)	4.794	258.6(0.01)	4.922	251.9(0.01)	5.100	243.1(0.05)
Methyl Propanoate								
LR-TD-B3LYP/6-311G(d,p)	3.805	325.8(0.10)	3.948	314.1(0.06)	4.116	301.2(0.01)	4.286	289.3(0.00)
LR-TD-B3LYP/TZVPP	3.753	330.4(0.10)	3.929	315.5(0.05)	4.122	300.8(0.01)	4.253	291.5(0.00)
LR-TD-CAM-B3LYP/6-311G(d,p)	4.628	267.9(0.02)	4.814	257.5(0.01)	4.935	251.2(0.00)	5.114	242.5(0.04)
LR-TD-CAM-B3LYP/TZVPP	4.550	272.5(0.03)	4.759	260.5(0.02)	4.897	253.2(0.00)	5.094	243.4(0.03)
Acetone								
LR-TD-B3LYP/6-311G(d,p)	3.881	319.5(0.09)	4.008	309.3(0.00)	4.195	295.5(0.01)	4.272	290.2(0.00)
LR-TD-B3LYP/TZVPP	3.835	323.3(0.08)	3.982	311.4(0.00)	4.190	295.9(0.00)	4.239	292.5(0.01)
LR-TD-CAM-B3LYP/6-311G(d,p)	4.615	268.6(0.01)	4.856	255.3(0.02)	4.497	250.6(0.00)	5.123	241.8(0.02)
LR-TD-CAM-B3LYP/TZVPP	4.542	273.0(0.01)	4.800	258.3(0.03)	4.904	252.8(0.00)	5.108	242.7(0.02)
Acetonitrile								
LR-TD-B3LYP/6-311G(d,p)	3.888	318.9(0.08)	4.023	308.2(0.00)	4.206	294.8(0.01)	4.268	290.5(0.00)
LR-TD-B3LYP/TZVPP	3.845	322.5(0.08)	3.996	310.3(0.00)	4.197	295.4(0.00)	4.238	292.6(0.01)
LR-TD-CAM-B3LYP/6-311G(d,p)	4.611	268.9(0.01)	4.864	254.9(0.02)	4.949	250.5(0.00)	5.131	241.6(0.02)
LR-TD-CAM-B3LYP/TZVPP	4.538	273.2(0.01)	4.808	257.9(0.03)	4.905	252.8(0.00)	5.111	242.6(0.01)