

COMPUTATIONAL AND EXPERIMENTAL STUDY OF PHOTOPHYSICAL PROPERTIES AND PROCESSES IN DYES AND SYSTEMS PMMA-DYES

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ABSTRACT

In the present study, five dyes, i.e., anthracene, aminoanthracene, perylene, 1,6-diphenyl-hexatriene and 7-diethylamino-4-methylcoumarin were studied in solvent and attached at the poly methyl methacrylate (PMMA) via DFT and TD-DFT calculations ^[1, 2]. Experimentally, micro and nano structures were developed through direct exposure of composites built out of these materials, with a diode laser system. The structures have systematically replicated specific geometry and features and are promising for nano-patterning applications.

Theoretically, in all PMMA-dyes, except for PMMA-perylen, fluorescence peaks in UV-vis area that correspond to electron transfer between PMMA and dyes were observed. On the contrary, in the case of PMMA-1,6-diphenyl-hexatriene, observed charge transfer from the dye to PMMA, but with small coordinator coefficient. Thus, we conclude that the ablation can occur to materials, while in the case of PMMA-1,6-diphenyl-hexatriene no photochemical response was observed resulting to the conclusion that the development of the structures can be attributed to a photothermal phenomenon.

KEYWORDS: dyes, poly-methyl-methacrylate, DFT, absorption and fluorescence spectra, micro and nano structures

EXPERIMENTAL STUDY

A direct laser writing setup was utilized to create ablation patterns on the surface of PMMA-dyes films with varying thicknesses. The setup employed a continuous wave Diode Laser operating at 405 nm. A high-magnification microscope objective lens with a numerical aperture of 0.9 enabled precise focusing. The samples were securely positioned on a motorized platform and could be moved along both the laser beam propagation z-axis for focus control and the perpendicular x-axis for parallel translation ^[3]. The PMMA-dyes films were prepared by spin-coating method.

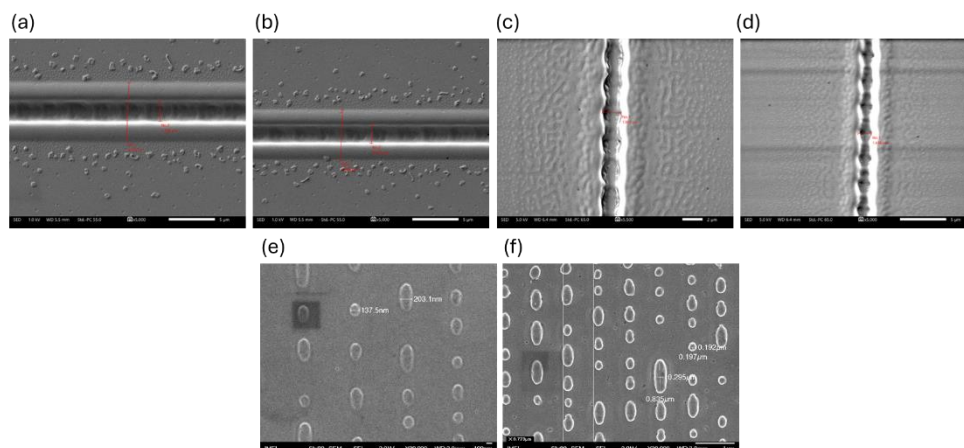


Figure 1. SEM images showcasing the results of direct laser writing in pigments of PMMA-dyes: (a) 8% w/v of Pe/thickness of film 1.2 μm /power of laser at 30 mW/swelling at 6.3 μm and ablation at 2.2 μm , (b) 8% w/v of Pe/thickness of film 1.2 μm /power of laser at 23 mW/swelling at 5.5 μm and ablation at 2.1 μm . (c) 30% w/v of Dm/thickness of film 850 nm/ power of laser 30 mW/ablation at 1.8 μm , (d) 30% w/v of Dm/thickness of film 850 nm/ power of laser 23 mW/ablation at 1.5 μm . (e) An and (f) Am observed no ablation phenomenon only berms development^{43]}.

COMPUTATIONAL STUDY

The calculations were performed using the B3LYP^[5] functional with the 6-31G (d, p)^[6] basis set in CHCl_3 solvent, employing the polarizable continuum model (PCM)^[7, 8]. The dielectric constant of CHCl_3 , $\epsilon=4.7113$, was considered, and all calculated molecular systems were found to be soluble in this solvent.

Initially, conformational analyses were conducted for the dyes, PMMA and PMMA-dye systems. All species were fully optimized energetically in the ground state to identify a global minimum structure for each. For the DFT calculations, the PMMA polymer was represented by a molecule with four repeating subunits. Subsequently, the absorption spectra of the studied structures were calculated using time-dependent DFT (TD-DFT) methodology in CHCl_3 solvent. In all cases, absorption spectra were calculated, encompassing up to 50 singlet and triplet-spin excited electronic states. These calculations were performed using the Gaussian16 code (<https://gaussian.com/>).

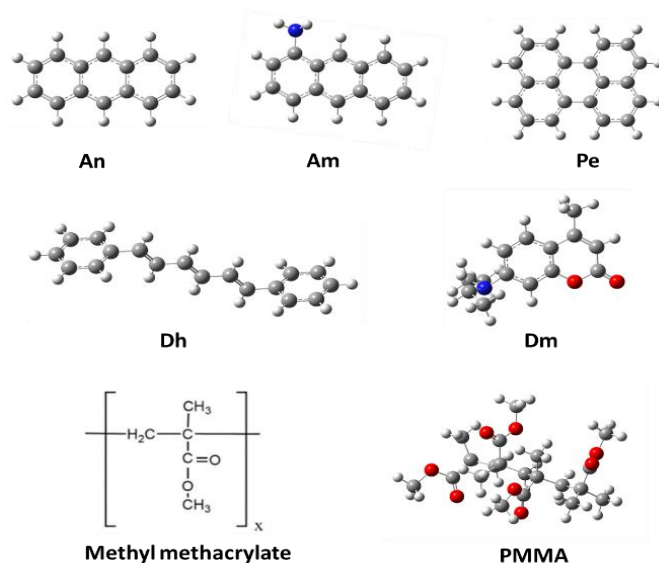

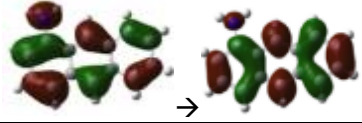
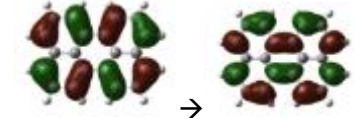

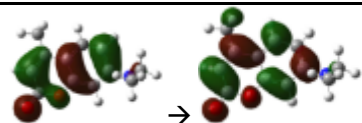


Figure 2. Molecule structures of calculated dyes: anthracene (An), aminoanthracene (Am), perylene (Pe), 1,6-diphenyl-hexatriene (Dh) and 7-diethylamino-4-methyl-coumarin (Dm), molecule structure of methyl

methacrylate, monomer of PMMA and the lowest in energy conformer of the model PMMA structure (3.63 kcal/mol). Grey balls=C atoms, white=H, red=O, and blue=N.

Table 1. Main absorption peaks λ (nm), Experimental λ (nm), Energy Differences ΔE (eV), f-Values, Excited State, Main MO Excitations and Frontier MO of dyes in CHCl_3 solvent.

Dye	λ	Experimental λ	ΔE	f	State	Coefficient	Main MO Excitation	Frontier MO
An	383.0	264.0	3.237	0.082	S_1	0.9921	$H \rightarrow L$	
Am	442.3	271.0	2.803	0.079	S_1	0.9911	$H \rightarrow L$	
Pe	441.7	435.0 254.0 207	2.807	0.477	S_1	0.9987	$H \rightarrow L$	
Dh	407.6	357.0	3.042	2.134	S_1	1.001	$H \rightarrow L$	
Dm	296.2	380.0 210.0	4.187	0.260	S_2	0.9369	$H-1 \rightarrow L$	

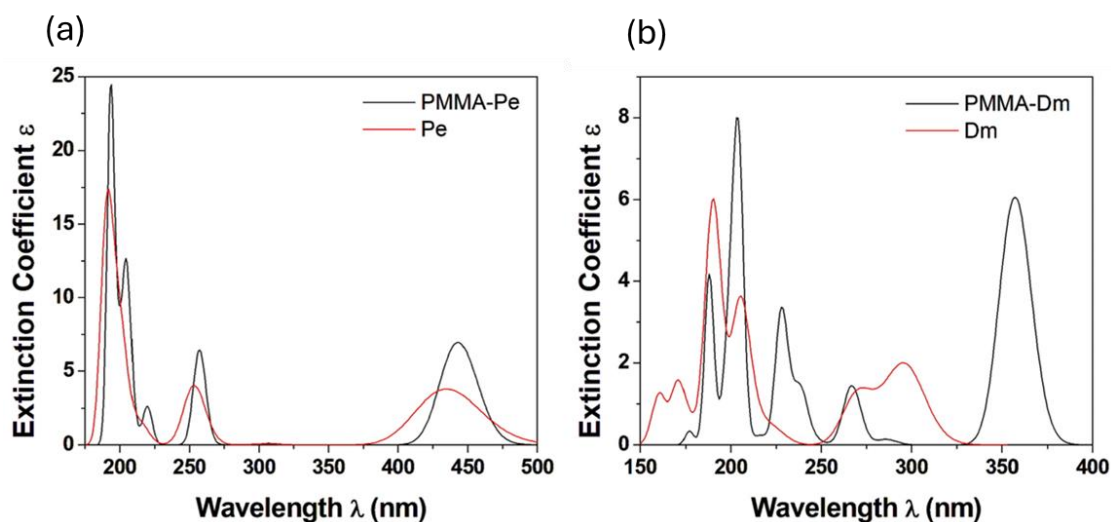
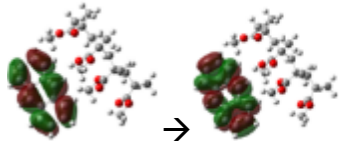
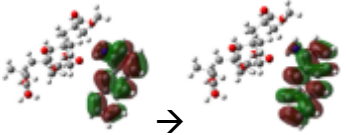
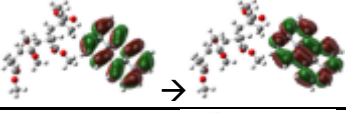

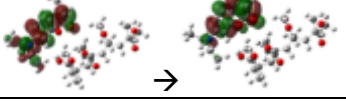


Figure 3. Absorption spectra of dyes and PMMA-dyes systems in CHCl_3 solution (a) Pe and pigment PMMA-Pe and (b) Dm and pigment PMMA-Dm.

Table 2. Main absorption peaks λ (nm), Energy Differences ΔE (eV), f-Values, Excited State, Coefficient, Main MO excitation and Frontier MO of PMMA-dye systems in CHCl_3 solvent.

PMMA-dye	λ	ΔE	f	State	Coefficient	Main MO excitation	Frontier MO
An	383.8	3.230	0.103	S_1	0.9921	$H \rightarrow L$	

Am	430.1	2.883	0.104	S ₁	0.9904	H → L	
Pe	443.4	2.796	0.517	S ₁	0.9986	H → L	
Dh	408.6	3.034	1.962	S ₁	1.001	H → L	
Dm	356.8	3.475	0.460	S ₁	0.9894	H → L	

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