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LIGHT ABSORPTION AND THERMAL PROPERTIES OF DENDRONIZED AZOCHROMOPHORES WITH BENZYL AND 2,3,4,5,6-PENTAFLUOROBENZYL FRAGMENTS

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Compounds, which could be useful for nonlinear optical applications, are dipolar push-pull chromophores and have large dipole moment; these molecules try to order themselves antiparallely decreasing the macroscopic electro-optical response due to centrosymmetric ordering [1]. One of the possibilities to help obtain ordered amorphous structures without centrosymmetry is arene-perfluoroarene (Ar-Ar^{F}) self-assembly in stacks due to quadrupolar interaction between electron-rich and electron-deficient aromatic rings [2, 3]. There are known molecular glasses containing small dendrons with phenyl and pentafluorophenyl moieties utilizing Ar-Ar^{F} interactions, which show increased electro-optical coefficients and orientation stability [3]. Our aim was to synthesize dendronized azobenzene chromophores and to investigate possible amorphous phase stabilization effects on them.

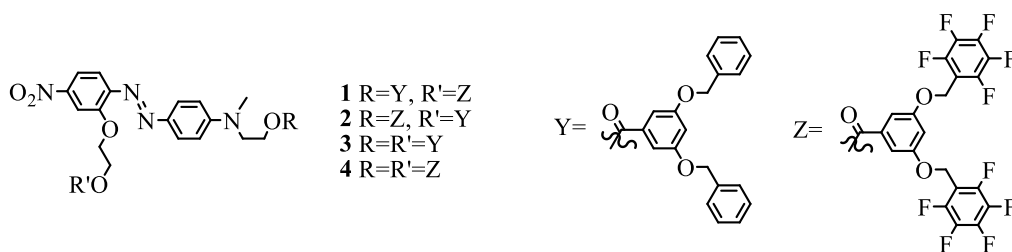


Fig. 1. Structures of dendronized azochromophores.

Syntheses of azochromophores **1-4** (Fig. 1) were performed from 2-(2-hydroxyethoxy)-4-nitroaniline, *N*-(2-hydroxyethyl)-*N*-methylaniline, 3,5-dibenzoyloxybenzoic acid and 3,5-bis(2,3,4,5,6-pentafluorobenzoyloxy)benzoic acid using azo-coupling reaction and ester formation reaction with *N,N'*-dicyclohexylcarbodiimide and 4-(dimethylamino)pyridine.

Compound	λ_{\max} , nm	λ_{\max} , cm^{-1}	ϵ , $\text{M}^{-1}\cdot\text{cm}^{-1}$	T_g , $^{\circ}\text{C}$	mp, $^{\circ}\text{C}$	T_d , $^{\circ}\text{C}$
1	478.9	20881	28944	53	147	250
2	480.2	20825	26563	58	70	260
3	479.1	20872	26792	47	130, 152	264
4	476.3	20995	32110	62	103	264
1 + 2				55	-	
3 + 4				55	139	

Table 1. UV-Vis spectra and thermal properties of compounds 1-4.

Light absorption maxima and intensity of all compounds in CHCl_3 solution (Table 1) were similar because the same azochromophore is used in the core of the molecule. Compound **4** had slightly different spectra than the other compounds; it had greater absorption intensity for about 16% and higher charge-transfer energy.

Two binary equimolar blends of azocompounds were prepared to investigate Ar-Ar^F interactions: compounds **1** and **2**, compounds **3** and **4**. Glass transition temperatures (T_g) showed that four 2,3,4,5,6-pentafluorobenzyl fragments of compound **4** increase T_g , but four benzyl fragments of compound **3** decrease T_g . Blends showed identical T_g which were about the average of their constituents. Compound **3** had two polymorphic modifications as indicated by two melting points (mp), blend **1 + 2** formed amorphous glass on evaporation, but blend **3 + 4** crystallized. Thermal stabilities of all compounds were very good as showed by 0.5% weight loss temperatures (T_d).

The effect of possible Ar-Ar^F interactions on thermal properties of synthesized compounds **1-4** was not observed, however the incorporation of only 2,3,4,5,6-pentafluorobenzyl fragments yielded higher glass transition temperature.

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