

Electronic Supplementary Information (ESI) for:

**Structure-Properties Relationship of Carbazole and Fluorene Hybrid Trimers:
Experimental and Theoretical Approaches**

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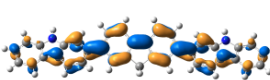
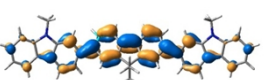
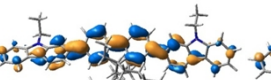
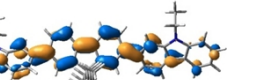
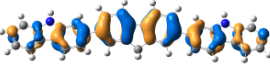

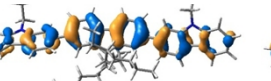
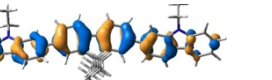
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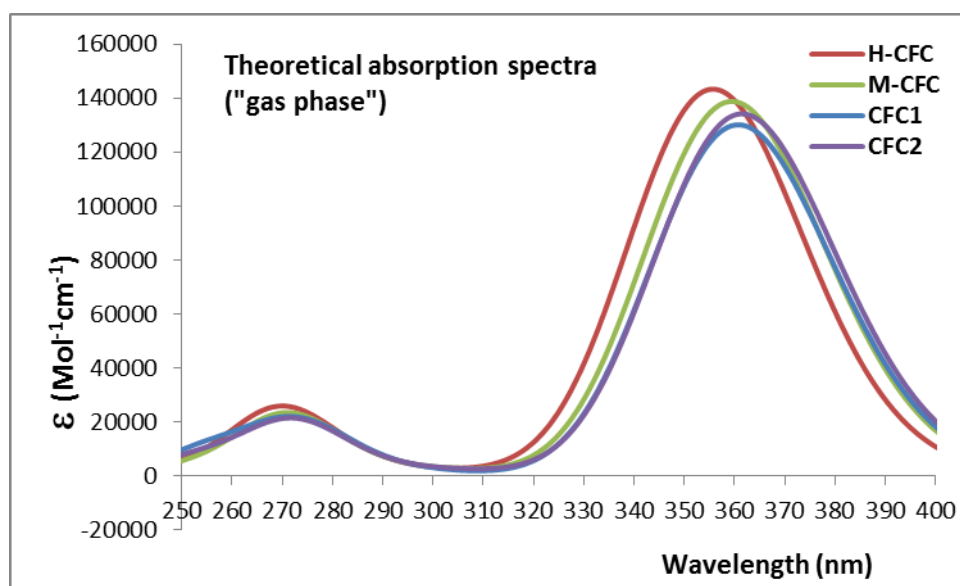
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Supplementary Information

	H-CFC	M-CFC	CFC1	CFC2
LUMO				
HOMO				
Gap(H-L) eV	3.88	3.85	3.84	3.83
Inter-core distance Å	1.484	1.484	1.484	1.484
Inter-core dihedral angle (degrees)	37.8	37.8	37.9	37.9

a



b

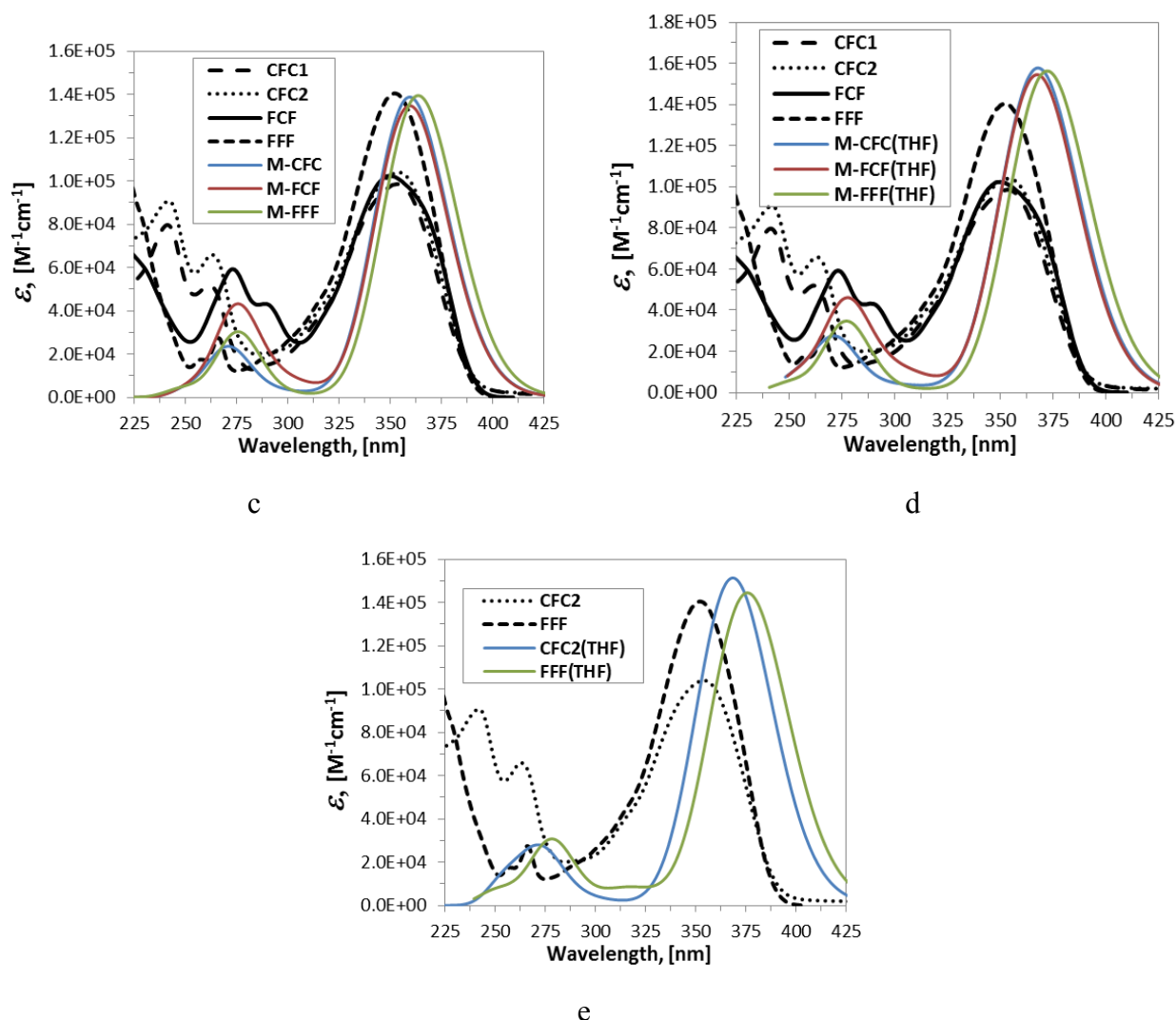


Figure S1. (a) HOMO and LUMO pictograms corresponding to H-CFC (containing hydrogen atoms instead of real alkyl groups), M-CFC (containing methyl groups instead of the real alkyl chains), and CFC1 and CFC2 (containing real alkyl groups), obtained at the B3LYP/6-31Gdp level in “gas phase”. The HOMO-LUMO gaps (eV) are indicated in parentheses. (b) Theoretical absorption spectra obtained by mean of TD/B3LYP/6-31Gdp calculations (“gas phase”), H-CFC, M-CFC, CFC1, and CFC2. The S_1 energies determined from the TDDFT calculations for H-CFC, M-CFC, CFC1, and CFC2 are 3.48 eV (356 nm), 3.45 eV (360 nm), 3.43 eV (361 nm), and 3.43 eV (362 nm) respectively. (c) Experimental absorption spectra of CFC1, CFC2, FCF, and FFF, and theoretical (TD/B3LYP/6-31Gdp, “gas phase”) absorption spectra of M-CFC, M-FCF, and M-FFF. (d) Same as in c), with the difference that the theoretical spectra are obtained by taking into account the effect of the solvent (THF). (e) Experimental (black curves) and theoretical (colored curves) absorption spectra of CFC2 and FFF (containing real alkyl chains).

The theoretical absorption bands are obtained by considering peak half-widths at half height of 0.2 eV.

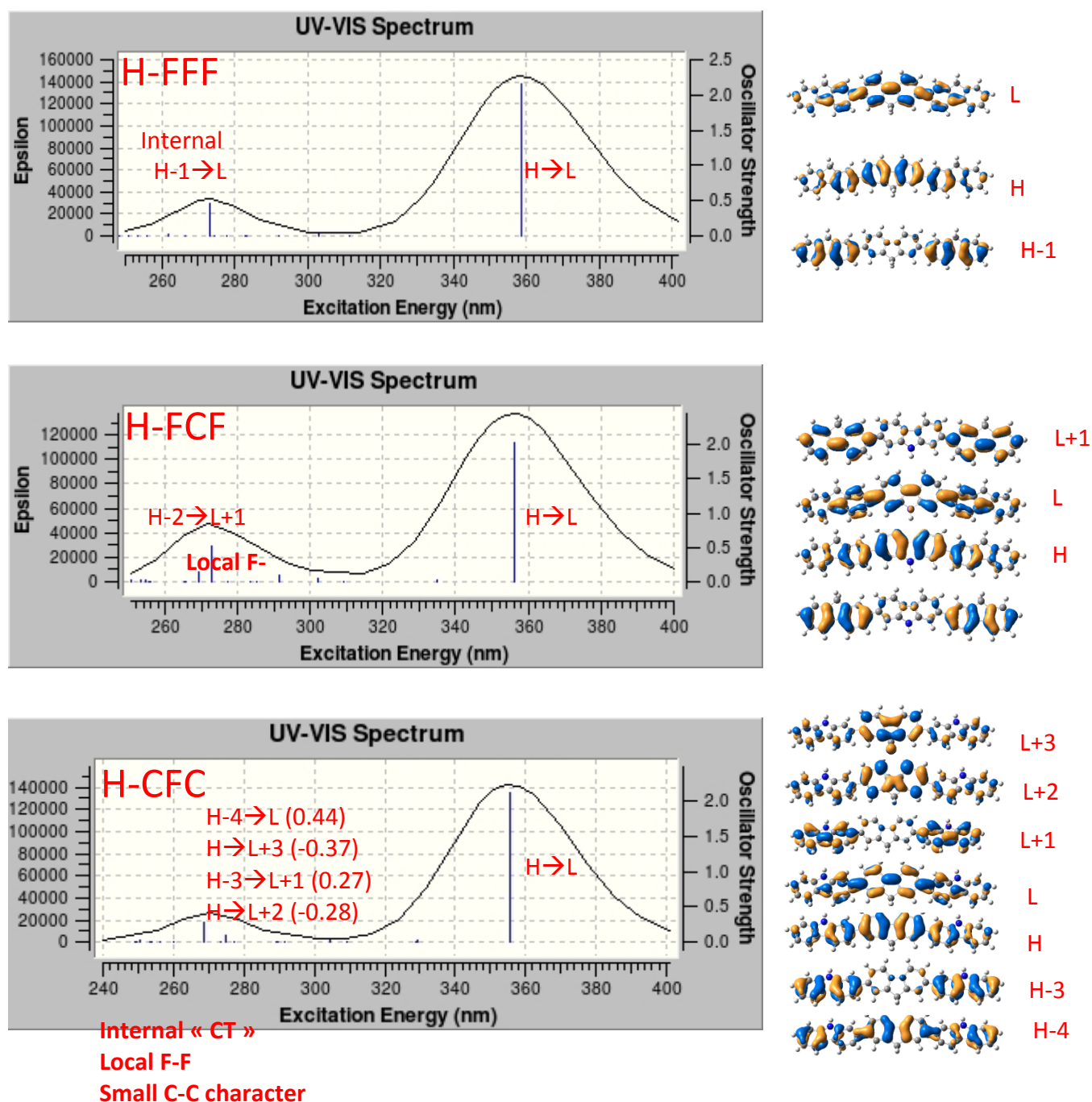
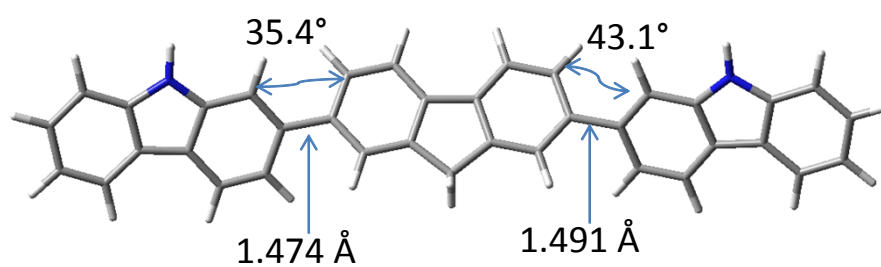
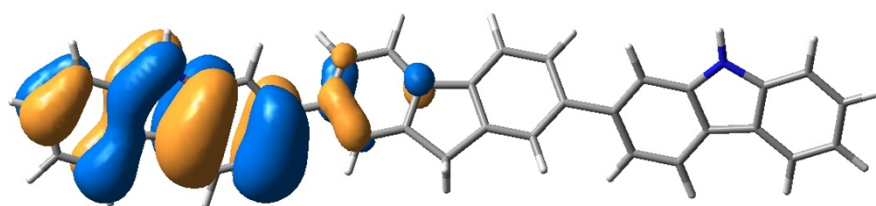


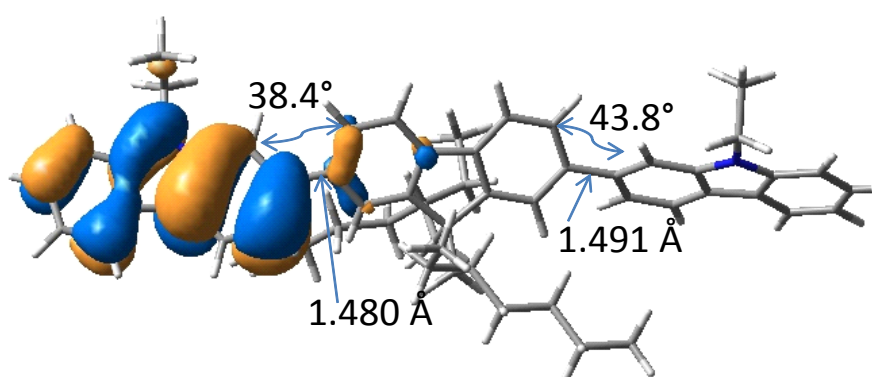
Figure S2. Theoretical absorption spectra of H-CFC, H-FCF, and H-FFF model compounds obtained by mean of TDDFT calculations at B3LYP/6-31G(d,p) level (in the absence of medium effects). The absorption bands are obtained by considering peak half-widths at half height of 0.2 eV. Some relevant MOs are also presented. In the case of the dominant transition corresponding to the high energy band of H-CFC, the individual transitions and their coefficients are indicated.



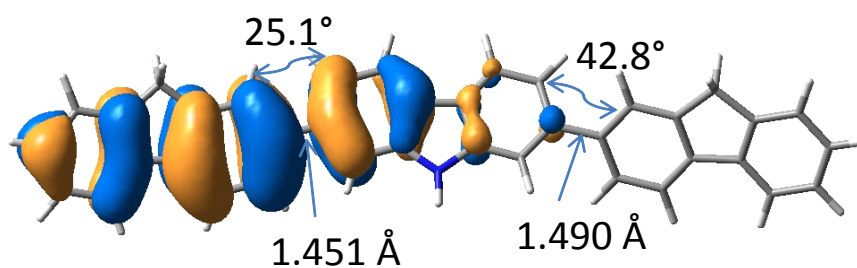
a



b



c



d

Figure S3. Theoretical (a) structure and (b) HOMO pictogram of cationic H-CFC model compound obtained at the roHF/6-31G(d,p) level calculation by taking into account the solvent effect (THF).

The geometrical parameters given in Fig.a correspond to the carbazole-fluorene distances and dihedral angles. Asymmetric geometry is obtained (Fig. a) resulting in localized HOMO (Fig.b). This structure is roughly 0.2 kcal.mol⁻¹ lower in energy than the corresponding symmetric structure. (c) Some relevant geometrical parameters and HOMO pictogram in the case of CFC1 (roHF/6-31G(d,p) in “THF”). Similar structural- and HOMO-distribution asymmetry wrt H-CFC can be observed. (d) Some relevant geometrical parameters and HOMO pictogram in the case of asymmetrical structure of H-FCF (roHF/6-31G(d,p) in “THF”).

A similar approach in the case of H-FCF (Fig.d) and H-FFF (not shown) results in asymmetric structures in both cases, being ~5.8 kcal.mol⁻¹ lower in energy and ~1.2 kcal.mol⁻¹ higher in energy respectively as compared to the corresponding symmetric ones.

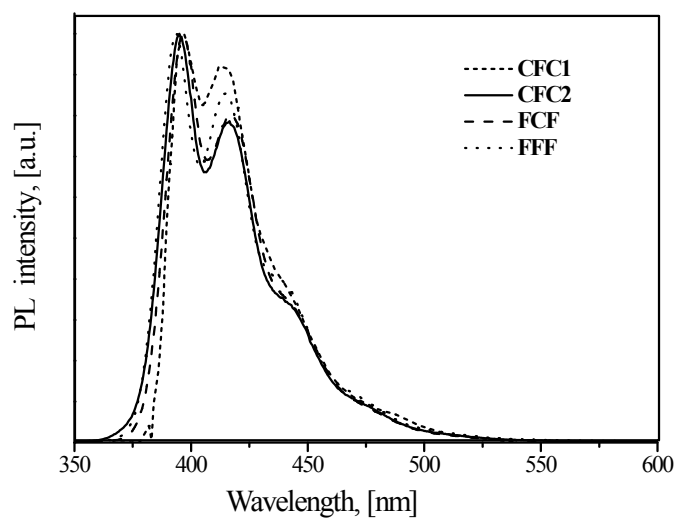


Figure S4. Normalized fluorescence spectra of the dilute (10^{-5} M) THF solutions of **CFC1**, **CFC2**, **FCF**, **FFF**.

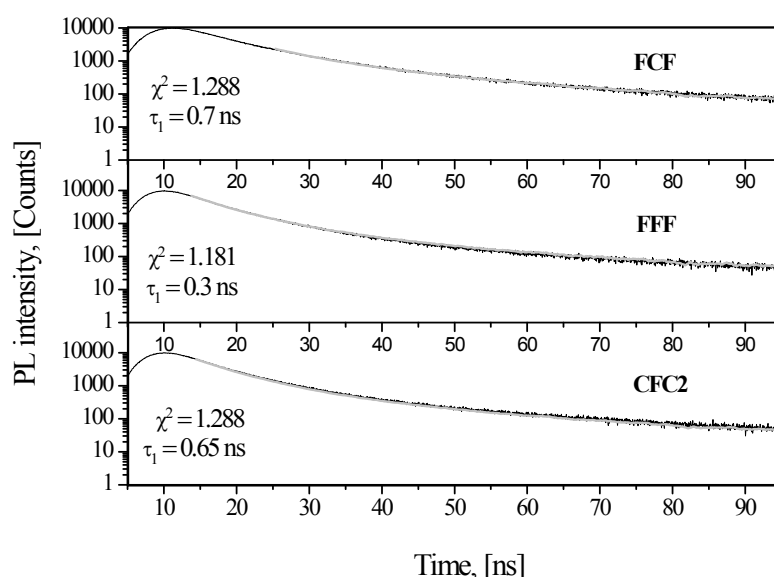


Figure S5. Fluorescence transients of dilute (10^{-5} M) THF solutions of **FCF**, **FFF**, and **CFC2**. Gray lines indicate single exponential fits of the experimental data. Fluorescence lifetimes (τ) are indicated.

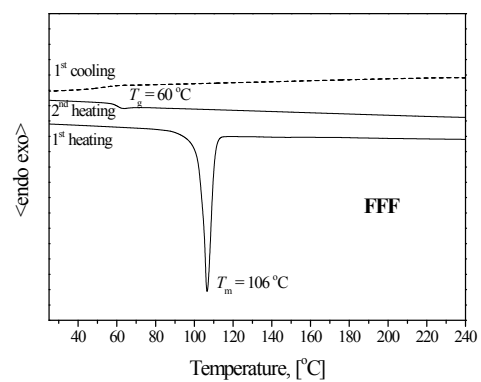
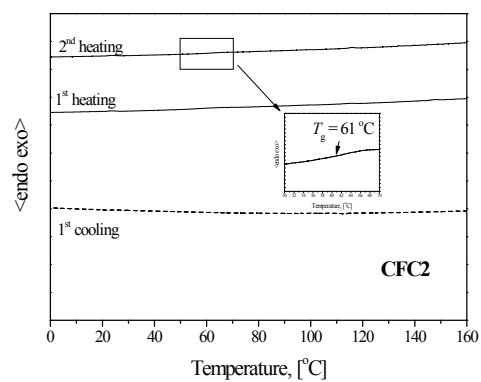


Figure S6. DSC curves of **FFF** and **CFC2** (heating rate $10\text{ }^{\circ}\text{C min}^{-1}$, N_2 atmosphere).

Table S1. Theoretical optical and electronic characteristics of **R-CFC**, **R-FCF**, and **R-FFF**, with **R= H, CH₃**, obtained at the **B3LYP/6-31G(d,p)** level “in gas phase”.

	$E(S_0 \rightarrow S_1)^a$		I_p^b		$\mathcal{E}^{\text{HOMO}}$		$\lambda_i^h,^c$		$\lambda_i^e,^c$	
	[nm]		[eV]		[eV]		[eV]		[eV]	
R	H	CH3	H	CH3	H	CH3	H	CH3	H	CH3
R-CFC	356	360	6.09	6.03	−5.17	−5.14	0.221	0.225	0.288	0.297
R-FCF	356	360	6.11	6.06	−5.19	−5.16	0.216	0.220	0.276	0.278
R-FFF	359	364	6.13	6.09	−5.21	−5.19	0.215	0.216	0.291	0.291

^a Theoretical $S_0 \rightarrow S_1$ absorption wavelengths. ^b Adiabatic I_p values. ^c Intramolecular reorganization energies for hole- and electron- transport.

Table S2. Dipole moment values (Debye) corresponding to **R-CFC**, **R-FCF**, and **R-FFF** (**R=H, CH₃**, Real), calculated at the **B3LYP/6-31G(d,p)** level “in gas phase” or in the presence of the solvent (THF) as indicated. “**R=Real**” means alkyl groups from the experimental structures.

R	R-CFC	R-FCF	R-FFF
H	2.8	1.0	0.7
CH ₃	3.3	1.2	0.6
Real-gas	2.9 (3.4) ^a	-	0.6
Real-THF	3.7 ^b	-	0.9

^a The values correspond to CFC1 et CFC2 respectively. ^b Corresponds to CFC1.

Table S3. Vertical and adiabatic T_1 energies of model compounds **R-CFC**, **R-FCF**, and **R-FFF**, **R=H, CH₃**, calculated with respect to the S_0 state by mean of TDDFT calculations at the **B3LYP/6-31G(d,p)** level “in gas phase” (values in parentheses correspond to **R=CH₃**).

	R-CFC	R-FCF	R-FFF
$T_1(v)$	2.60 (2.57)	2.62 (2.59)	2.55 (2.52)
$T_1(ad)$	2.23 (2.20)	2.29 (2.27)	2.20 (2.17)