Tuning J-aggregate Formation and Emission Efficiency in Cationic Diazapentacenium Dyes

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Abstract: Enhancement of the luminescence efficiency of two new diazapentacenium salts (**D1** and **D2**) of more than 55 for **D1** and 22 times for **D2**) in poor solvents, acetonitrile and/or dichloromethane, was observed and rationalized as formation of emissive J-aggregates. Both compounds displaying 4-*n*-decylphenyl substituents at the 7,14-carbons and phenyl (**D1**) or 2,6-difluorophenyl (**D2**) substituents at the quaternary nitrogen atoms in 5,12-positions have been synthetized in a two-step procedure involving a two-fold Buchwald-Hartwig-type CN cross-coupling and an electrophilic Friedel-Crafts-type cyclization. The optical properties of the dicationic diazapentacenium salts in various solvents and in thin films have been investigated by steady-state and time-resolved absorption and photoluminescence spectroscopies. In thin films and in good solvents, isolated molecules coexist with aggregates. Nonetheless, **D1** is seven times more emissive than **D2**, reflecting a higher J-aggregate contribution in the former.

Since John and Clar's synthesis of pentacene in the early 1930's,[1] the synthetic strategies and properties of higher member acenes have challenged chemists. Early on, pentacene and structurally related molecules were of curiosity-driven research; nowadays, pentacene is considered a reference hole semiconductor in organic field-effect transistors.[2] Propelled by such curiosity, boron and nitrogen atoms have been introduced into π-backbones of poly-aromatic hydrocarbons, structurally similar to their hydrocarbon analogues, resulting in interesting

heteroarene molecules showing different properties.[3] Azapentacenes are, thereby, a particularly interesting subgroup of these heteroarenes,[3a] which formally result from inserting nitrogen atoms into the pentacene skeleton; such interest mainly arose from the promise of tuning the electronic structure, molecular packing, stability, and processability of pentacene by replacing C atoms with N atoms of varied number, position and valence state.[4] Synthetic routes to prepare azaacenes often use condensation/alkynylation methods that have been developed for the preparation of all-carbon-acenes.[5] Known N-quaternized azaacenium salts were synthesized by N-alkylation of azapentacenes or by introducing aryl groups into the precursors of azaacenes.[6] *N,N'*-dihydro compounds, which may be obtained by reduction of larger azaacenes, are known for much longer time, and found more stable than longer azaacenes themselves.[7]

Aggregation induced emission (AIE) and AIE-luminogen systems are, at the moment, topics of high interest and impact due to the increment of the emission properties in aggregate systems, which are usually poorly emissive. The occurrence of AIE with a new fluorescence band originating from intermolecular interactions was first reported by Scheibe *et al.*[8] and Jelley[9] who independently observed in 1936 an unusual behavior for pseudoisocyanine chloride (also known as 1,1'-diethyl-2,2'-cyanine chloride, PIC chloride) whereas in aqueous solutions the absorption maximum was shifted to lower energies, when compared to the absorption spectrum of the same dye in ethanol, and upon concentration increase (in water), this band became more intense and sharp.[10] Dye aggregates with a narrow absorption band bathochromically shifted, with a very small Stokes' shift and increased fluorescence intensity relative to the monomer are generally termed Scheibe aggregates or J-aggregates (*J* denotes *Jelley*).[11] In contrast, aggregates with absorption bands shifted to shorter wavelength (hypsochromically shifted) with respect to the monomer band are called H-aggregates (H denotes hypsochromic), in most cases coupled to the occurrence of low intensity, or absence of fluorescence.[12]

Currently, AIE or aggregation induced enhanced emission (AIEE) caused by the formation of J-aggregates have been described in several systems. Oelkrug *et al.* has demonstrated the role of J-aggregation for enhanced solid-state emission of a series of oligophenylene vinylenes, with the increase of fluorescence quantum yield from almost zero in solution to 60% in nanoparticles or in films.[13] They explained this phenomenon as arising from the rigid environments provided by viscous solvents or solid phases that suppress torsion-induced radiationless deactivation.[14] In this work, we report, to

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our best knowledge, for the first-time the formation of J-aggregates in quaternized 5,12-diazapentacenium salts, coupled to an increase in fluorescence intensity (AIE properties).

For synthesis of the diazapentacenium salts, N,N'-diaryl$_1$-N,N'-diaryl$_2$-substituted 2,5-bis(4-n-decylbenzoyl)-1,4-phenylene diamine precursors (aryl$_1$: 4-n-decylphenyl, aryl$_2$: phenyl (**D1**) or 2,6-difluorophenyl (**D2**)) were generated in Buchwald-Hartwig-type aryl-amine couplings (Scheme 1). The Friedel-Crafts-acylation-type cyclization chemistry was already reported for synthesis of monocationic N-arylacridinium salts, specifically for reaction of triphenylamines with benzoic acid derivatives or cyclization of 2-benzoyltriphenylamine into 9,10-diphenylacridinium salts, both at (nearly) quantitative conversion of the starting compounds into the respective products.[15]

The photophysical properties of the diazapentacenium salts **D1** and **D2** (Scheme 1) were studied in five solvents of different polarity (here given as solvent's relative permittivity, ε): two low polarity aprotic solvents, tetrahydrofuran (THF, ε = 7.58), and dichloromethane (DCM, ε = 8.93) and acetonitrile (ACN, ε = 37.5) as polar aprotic solvents, and methanol (MeOH, ε = 32.7) as polar protic solvent. Thin films of the diazapentacenium salts prepared by spin-coating supported in zeonex matrices were also studied. Absorption, fluorescence emission and excitation spectra for the two compounds **D1** and **D2** are depicted in Figure 1. A first visual observation shows that the solution colour strongly depends from the solvent used (Figure S1 and Table S1). However, in DCM and ACN very similar solution colours for both compounds are observed. In other solvents,

also significant differences between **D1** and **D2** are noticed (see Figure S1).

MeOH for **D1** and THF for **D2** represent the best solvents for each compound. The difference between **D1** and **D2** is expected to be caused by the introduction of the fluorine atoms into the N-phenyl substituents. Here, absorption and emission, associated to a π-π* transition, lack vibronic resolution and the compounds are practically non-emissive, with $\phi_F \leq 1\%$ (Table 2). In contrast, ACN and DCM, behave as a poor solvent for the two salts. Now, mirror-symmetry between absorption and fluorescence excitation spectra is observed. Especially **D1** is much more emissive in ACN and DCM if compared to MeOH as good solvent (see the ϕ_F values in Table 2). The long-wavelength absorption bands are vibronically resolved and red shifted, when compared to the spectra in the good solvents MeOH and THF at the same concentrations. For similar cationic compounds, e.g., quaternary N-phenyl azaacenium salts in dichloromethane, also small Stokes' shifts and vibronically well-resolved long wavelength absorption bands have been reported.[7] The formation of the vibronically structured, red shifted absorption bands, together with a small Stokes' shift ($\Delta_{SS} \sim 600$ cm^{-1}, Table 1) and an increase of the fluorescence quantum yield (ϕ_F), indicates the formation of J-aggregates in the poor solvents ACN and DCM (Figure 1). In thin films, although the longest absorption and emission bands are vibronically resolved for **D1**, the ϕ_F value is lower than in poor solvents but higher than in good solvents (Table 2). For thin films of **D2**, a broad absorption and emission bands are
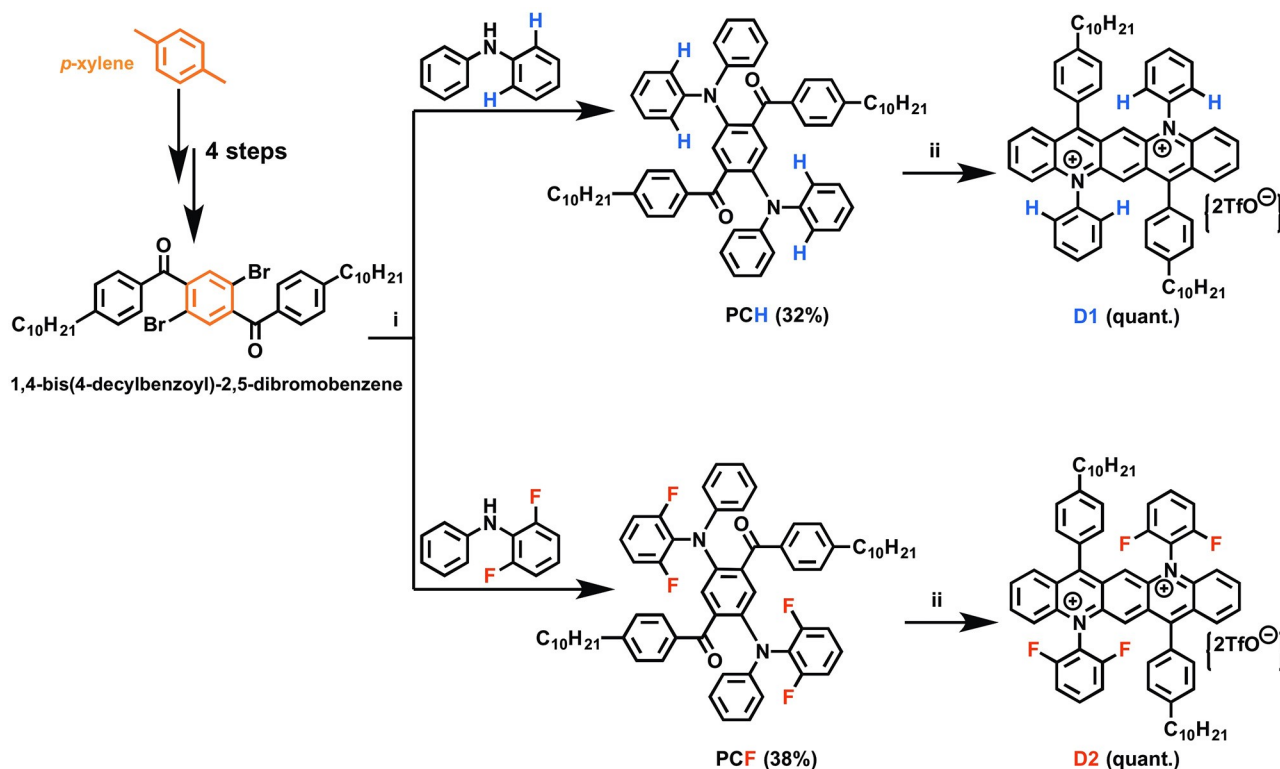
Scheme 1. Synthetic route to the diazapentacenium salts **D1** and **D2**. i) NaO-t-Bu, Pd(OAC)$_2$, tri-t-Bu-phosphine, toluene, 120 °C, 16 h; ii) trifluoromethanesulfonic acid (TMSA) under argon, toluene, 50 °C, 3 h.

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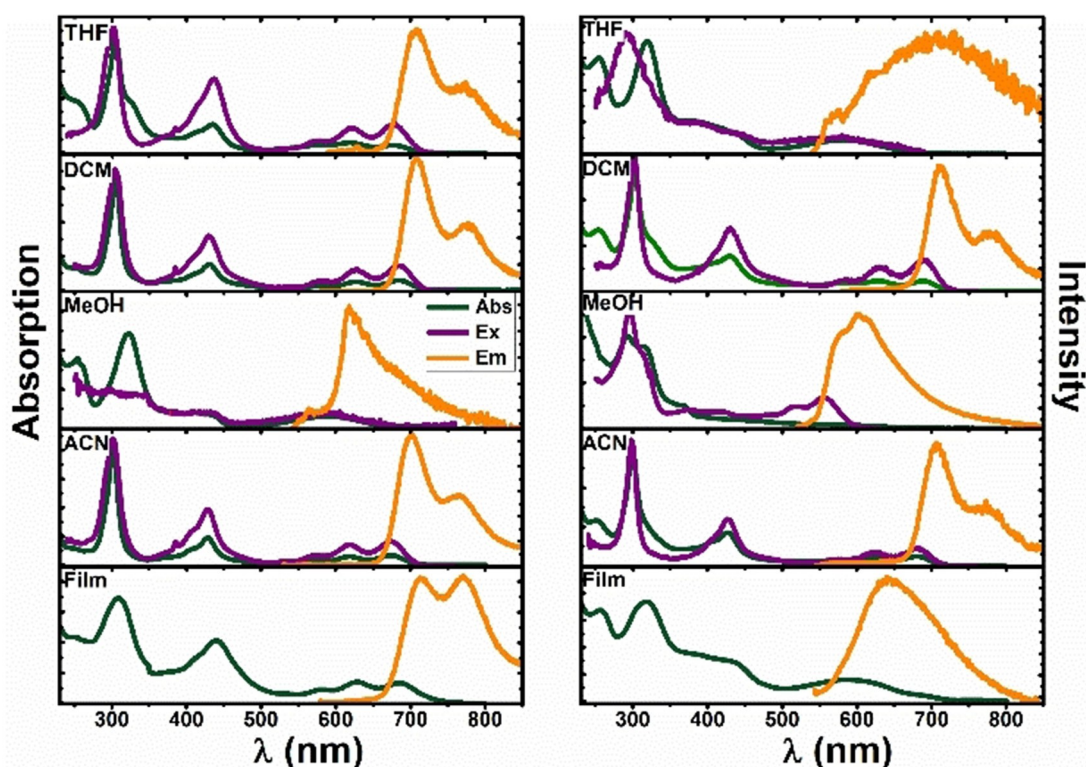Europe
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Figure 1. Absorption, fluorescence excitation, and emission spectra of compounds **D1** (left) and **D2** (right) in THF, DCM, MeOH, ACN and in films. All spectra were recorded with concentration $= 1.0 \times 10^{-5}$ mol L^{-1}. Abs $=$ absorption spectra; Ex $=$ excitation spectra; Em $=$ emission spectra.

Table 1. Spectroscopic data (Absorption, λ^{abs}, emission maxima, λ^{em}, and Stokes shift, Δ_{SS}) of diazapentacenium salts **D1** and **D2** in different solvents.[a]				
Dye	Solvent	λ^{abs} [nm]	λ^{em} [nm][b]	Δ_{SS} [cm^{-1}]
D1	THF	304/435/575/620/678	708/773(s)	625
	DCM	305/431/581/627/685	709/773(s)	494
	MeOH	323/411/589	683	2337
	ACN	302/428/569/618/674	701/765(s)	571
	Film	309/440/580/630/685	713/770	573
D2	THF	319/386/583	716	3186
	DCM	302/429/581/628/688	710/778(s)	450
	MeOH	317/384/555	572/618(s)	536
	ACN	300/427/576/620/680	709/773(s)	602
	Film	318/379/430/586	642	1489
[a] All data were collected with a concentration $= 1.0 \times 10^{-5}$ mol L^{-1}. [b] Emission maxima were collected with with excitation into the S$_0 \rightarrow$ S$_1$ band ($\lambda^{ex} = 530$ nm). s $=$ shoulder.				

observed, with a large Stokes shift and low ϕ_F value. The data indicate that the C$_{10}$H$_{21}$ chain (present in **D1** and **D2**) and the fluorine atoms (only in **D2**) contribute differently to the degree of organization of the salts in the solid state and in solutions of poor solvents. To summarize at this stage, a comparison of all spectra for **D1** and **D2** shows significant differences for the solutions in different solvents, but also some differences between **D1** and **D2**: THF is a good solvent for **D2**, but not for **D1**, while MeOH is a good solvent for **D1** (Figure 2).

The observed spectral characteristics for **D1** or **D2** in ACN and DCM (especially for the absorption and fluorescence excitation spectra) together with the red shifted fluorescence and increased quantum yields, ϕ_F, indicates J-aggregate formation in these poor solvents. However, the most attractive

feature comes from the distinct increase, by 55 times (for **D1**) and 22 times (for **D2**) in ϕ_F when going from the good solvents to ACN as poor solvent (**D1**: MeOH$\rightarrow$ACN; **D2**: THF$\rightarrow$DCM).

Next, we varied the concentrations of **D1** and **D2**; the results (concentration range from 2.0 to 50×10^{-6} mol L^{-1}) show that **D1** (Figure S2) and **D2** (Figure S3), both in THF or ACN, display similar spectral profiles during the variation of the concentration, with the intensities of absorption, fluorescence excitation and emission linearly increasing with increasing concentration (Figures S2 and S3).

However, for **D2** in MeOH (Fig. S3), the spectral profile changes, and the intensity of the observed bands does not linearly respond to an increasing concentration, as indication for the presence of mixtures of different absorbing/emitting

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Table 2. Room temperature fluorescence quantum yields (φ_F) and emission lifetimes[a] (τ_i) for compounds **D1** and **D2** in pure solvents. Also presented are the associated pre-exponential factors (a_i), the fractional contributions for each decay time (%C_i), and the chi-square values (χ^2) for the judgment of the quality of the fits. Radiative (k_F) and radiationless rate (k_{NR}) constants associated with the third decay component (τ_3) are also listed.

Dye	Solvent	Concentration [μM]	φ_F	τ_1 [ns]	a_1 [C_1%]	τ_2 [ns]	a_2 [C_2%]	τ_3 [ns]	a_3 [C_3%]	χ^2	[b]$k_F \times 10^{-6}$ [s^{-1}]	[c] $k_{NR} \times 10^{-8}$ [s^{-1}]
D1	THF	50	0.013					4.07	1 (100)	0.69	3.19	2.43
	DCM	50	0.102					5.41	1 (100)	0.81	18.9	1.66
	MeOH	50	0.002	0.16	0.889 (44)	1.18	0.096 (35)	4.40	0.015 (21)	1.04	0.46	2.27
	ACN	50	0.11					4.36	1 (100)	0.70	25.2	2.04
	Film	–	0.007	0.14	0.968 (50)			4.27	0.032 (50)	1.09	1.64	2.36
D2	THF	50	0.001	0.34	0.902 (62)	1.51	0.089 (27)	5.65	0.010 (11)	0.92	0.18	1.77
	DCM	50	0.022	1.21	0.146 (5.5)			3.55	0.854 (94.5)	0.68	6.2	2.75
	MeOH	5	0.067			13.31	0.026 (7.0)	4.56	0.974 (93)	1.16	14.7	2.05
		10	0.018			13.30	0.028 (8.0)	4.5	0.972 (92)	1.04	4.0	2.18
		25	0.003	0.42	0.894(30)	18.65	0.025 (37)	5.03	0.081 (33)	1.01	0.60	1.98
		50	0.001	0.48	0.797 (22)	21.21	0.019 (24)	5.02	0.184 (54)	1.11	0.20	1.99
	ACN	50	0.008					2.36	1 (100)	0.6	3.4	4.20
	Film	–	0.001	0.19	0.996 (92)			4.17	0.004 (8)	0.82	0.24	2.40

[a] Experimental conditions: $\lambda^{ex} = 460$ nm [b] $k_F = \frac{\phi_F}{\tau_F}$. [c] $k_{NR} = \frac{1-\phi_F}{\tau_F}$.
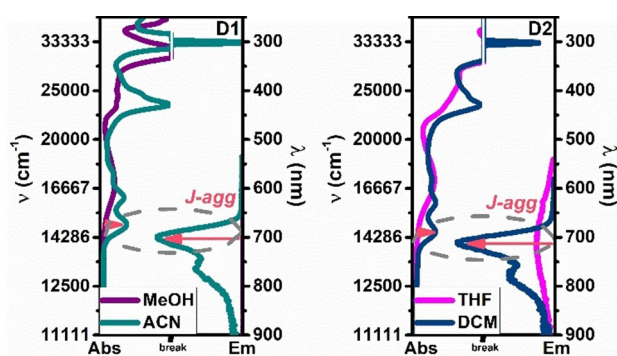

Figure 2. Absorption and emission spectra of compounds **D1** and **D2** in good and poor solvents pairs. [**D1**, **D2**]: 1.0×10^{-5} mol L^{-1}. Highlighted bands were assigned to J aggregates (J-agg) of **D1** and **D2**. Line breaks were added to magnify visualization of the new absorption bands (at lower wavenumbers) present in poor solvents.

species (isolated molecules, aggregates). The ϕ_F also decreases with the concentration (Table 2). At the lowest concentration (2 μM), the emission spectrum is poorly resolved (presence of isolated, non-aggregated molecules), whereas at 5 μM the spectrum displays the characteristic (vibronically structured) emission of either **D1** or **D2** J-aggregates observed in poor solvents such as DCM and ACN. Further increase in concentration leads, best seen in the fluorescence excitation spectra, to a progressive loss of the vibronic resolution and the appearance of an additional broad emission band at emission wavelengths > 700 nm, that increases in intensity with increasing concentration. We attribute this behaviour to an initial coexistence of monomers and, possibly, a few J-aggregates at low concentrations, with the relative concentration of J-aggregates increasing with increasing concentration and reaching its maximum for a concentration of ca. 5 μM. Further increase of the concentration leads to the progressive formation of disordered and/or ill-defined, non-emissive aggregates, reflected in a gradual decrease of ϕ_F with the rise in concentration for **D2** in MeOH.

To further rationalize these observations, time-resolved studies were performed (Figure S4 and S5). The complete photophysical data (quantum yields and decay times) of the two compounds in different organic solvents and in films, together with the concentration dependence for **D2** also in methanol, are presented in Table 2.

In DCM and ACN, the emission of both **D1** and **D2** decays mono-exponentially with lifetimes $\tau = 5.41$ ns (DCM) and 4.36 ns (ACN) for **D1**, and $\tau = 3.55$ ns (DCM) and 2.36 ns (ACN) for **D2**. This emission behaviour is assigned to J-aggregates. Also in THF, as poor solvent for **D1**, a single-exponential decay ($\tau = 4.07$ ns) is observed, indicative of J-aggregation. In MeOH (for **D1**) and THF (for **D2**), as good solvents, it seems that, a few amount of aggregated species coexist with the monomeric component (showing the shortest lifetime of $\tau_1 < 1$ ns). As expected, **D1** and **D2** show the lowest ϕ_F in these solvents. In MeOH, **D2** displays a much higher lifetime decay component ($\tau_2 > 13$ ns). The contribution associated to this lifetime increases with increasing concentration, accompanied by the occurrence of an additional emission band at longer wavelengths, at > 700 nm, and by an ongoing fluorescence quenching (Figure S3). In thin films, the fluorescence decays for **D1** and **D2** are bi-exponential, showing that both monomers and J-aggregated coexist, yet with different contributions. Indeed, for **D1** J-aggregates and monomers are found with equal contribution to fluorescence (as seen by the %C1 and %C3, in Table 2), whereas for **D2**, J-aggregates contribution is now of 8%. These findings corroborate the steady-state data with **D1** presenting higher ϕ_F values (higher J-aggregate contribution), while **D2** is poorly emissive in the solid state (lower J-aggregates contribution). The radiative (k_F) and non-radiative rate (k_{NR}) constants were determined by considering the lifetime τ_3 as indicator of J-aggregate formation. The k_{NR} are at least 1 order of magnitude higher than k_F in solvents where the compounds show a higher ϕ_F. The photophysical data (Table 2) also display an increase in the radiative rate constant (when going from good to poor solvents) of more than one order of magnitude with a nearly constant rate constant of radiation-less deactivation. For **D1**, as example, k_F goes from 0.5×10^6 s^{-1} to 25×10^6 s^{-1} (MeOH→ACN),

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whereas k_{NR} only varies between $2.3 \times 10^8 \, s^{-1}$ and $2.0 \times 10^8 \, s^{-1}$ in these solvents. This also reflects the enhancement of the photoluminescence emission intensity caused by J-aggregate formation.

We hereby describe the synthesis and optical characterization of two cationic diazapentacenium dyes, with particular emphasis to the photoluminescence properties in different solvents. Our data indicate formation of emissive J-aggregates in poor solvents, while in good solvents and in thin films, isolated molecules coexist with aggregates. This is evidenced by a strong increase of the fluorescence quantum yields along with the appearance of a narrow absorption band bathochromically shifted in poor solvents. Therefore, the nature of the fluorescence decay changes from single exponential (when J-aggregates dominate, in poor solvents) to triexponential decays, reflecting the coexistence of isolated molecules, J-aggregates, and, probably, other disordered aggregate species; the last presented especially at higher concentrations. The simple structural change of the N-aryl substituents from phenyl (**D1**) to 2,6-difluorophenyl (**D2**) also influences the optical properties. As an example, THF is found to be the best solvent for fluorinated derivative **D2**, while it is a poor solvent for **D1**. This illustrates that simple structural modifications in these compounds can dramatically change their optical properties, thus paving the way for a rational control of the supramolecular ordering, and consequently, of the luminescence efficiency.

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Conflict of Interest

The authors declare no conflict of interest.

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