Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.
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Electronic Supplementary Information

Increased luminescence efficiency by synergistic exploitation of lipo/hydrophilic co-solvency and supramolecular design

Giulia Tregnago, Michele Serri, Sergio Brovelli, Shane O. McDonnell, Platon Korniychuk, Linjun Wang, Michael Wykes, David Beljonne, Adam Tracz, Harry L. Anderson, Franco Cacialli

Summary

a. Experimental and computational details

The synthesis and characterization of sulfonate substituted poly(diphenylene-vinylene) lithium salt (PDV.Li) and its cyclodextrin polyrotaxane derivative (PDV.Li⊂β-CD, with a threading ratio of 2 cyclodextrins per repeat unit) used in this work is described elsewhere[1].

All data shown were taken for PDV.Li and PDV.Li⊂β-CD solutions in water/propanol mixtures at a concentration of $5x10^{-3}$ mg·mL^{-1} and $1.1x10^{-2}$ mg·mL^{-1} respectively, in order to account for the different molecular weight and obtain the same optical density. Solutions were prepared from a "master" solution in water, i.e. 1

mg·mL^{-1} and 2.2. mg·mL^{-1}, for PDV.Li and PDV.Li⊂β-CD respectively, then diluted 200 times. Therefore, solutions with the highest content of propanol contain 0.5% of water. Optical absorption spectra were collected in the visible and near-ultraviolet (UV) region by means of a CCD-based spectrophotometer (Agilent 8543) with a spectral resolution of 1 nm. Decay dynamics were studied with a time-correlated single-photon counting (TCSPC) spectrometer using a ps-pulsed diode laser at 371 nm (Edinburgh Instruments EPL-375) and a F-900 TCSPC unit (temporal resolution ~150 ps) with a photomultiplier tube coupled to a monochromator.

The PLQE were measured using a relative method for optical dilute solutions, using as reference the quantum yield of quinine sulfate dehydrate in 1.0 N sulfuric acid (~10^{-5} M; PLQE = (0.546 ± 5 %) (NIST standard reference material SRM# 936a (www.nist.gov/ts/msd/srm/)). Refractive indices for water/1-propanol mixtures (see Table 1) were taken from data reported in the literature. [2, 3]

Table S1 Extrapolate refractive indices for water/1-propanol mixtures from references [2, 3]

Water content (%)	Refractive index
100	1.333
90	1.340600734
80	1.348325645
70	1.35499813
50	1.365760976
30	1.375439499
20	1.379749526
8	1.383248019
5	1.383971197
0.5	1.385075773
0	1.3852

All experiments were performed at room temperature and all measurements were corrected for the overall spectral response of the detector.

Optimized ground-state geometries and excited state calculations of model aggregates of PDV.Li and PDV.Li⊂β-CD are shown in Figure S4. Lithium ions are assumed to be dissociated, as is likely the case in water. Each sulfonate group thus adds a charge of -1 to each chain. By adopting a geometry in which neighboring chains are offset with respect to each other along the long polymer axis, the distance between sulfonates is maximized, minimizing the coulomb repulsion between them such that it does not hinder the close packing of PDV.Li chains at ~3.5-3.6 Å. In PDV.Li⊂β-CD, the supramolecular encapsulation provided by β-CD increases this distance to 8.5-9 Å. The ground-state geometry of the PDV.Li model aggregate was optimized at the wB97XD/6-31g(d) level, including a Polarizable Continuum Model (PCM) description of solvent effects using default parameters for water, as implemented in Gaussian09 RevA.02.[4] As it would have been computationally impractical to perform a similar calculation on the ground-state geometry of PDV.Li⊂β-CD, semi-empirical method including dispersion and hydrogen bonding corrections for PM6-DH was instead used, as implemented in MOPAC2009.[5] ZINDO/SCI calculations and all simulations of spectra were performed with in-house codes. Details of the precise Frenkel-Holstein model and Hamiltonian employed in the phenomenological spectral simulations have been reported elsewhere.[6] Briefly, as we are only interested in the low energy part of the optical absorption spectra, we assume that each chromophore in the aggregate has only two electronic states; the ground state (S_0) and the first excited state (S_1), which are coupled to an intramolecular symmetric vinyl-stretching mode, and that chromophores within the aggregate interact only with their nearest neighbours, with a constant excitonic coupling term. Our parameterization strategy was as follows; we first simulated an isolated PDV.Li molecule with a single-mode Franck-Condon progression (equivalent

to the Frenkel-Holstein model with the excitonic coupling set to zero) with up to four vibrational quanta. Hand tuning of the parameters to provide the best agreement with the observed emission spectrum of PDV.Li in 50% water (believed to arise mainly from single-chain emission) yielded the following experimentally-derived parameters: A S_0-S_1 0-0 transition energy of 2.78 eV, an effective vibrational energy of 0.17 eV (~1400 cm^{-1}), a Huang-Rhys factor 1.17 and Gaussian broadening with σ = 75 meV (FHWM ~180 meV). Having fixed these parameters, spectra of model aggregates comprising 10 interacting chromophores were simulated with various values of the excitonic coupling. Simulations made use of the two particle approximation and a maximum vibrational quantum number of four at a temperature of 300 K. No energetic disorder in site energies was employed in order to avoid overfitting of the spectrum with the addition of further parameters.

b. Absorption spectra

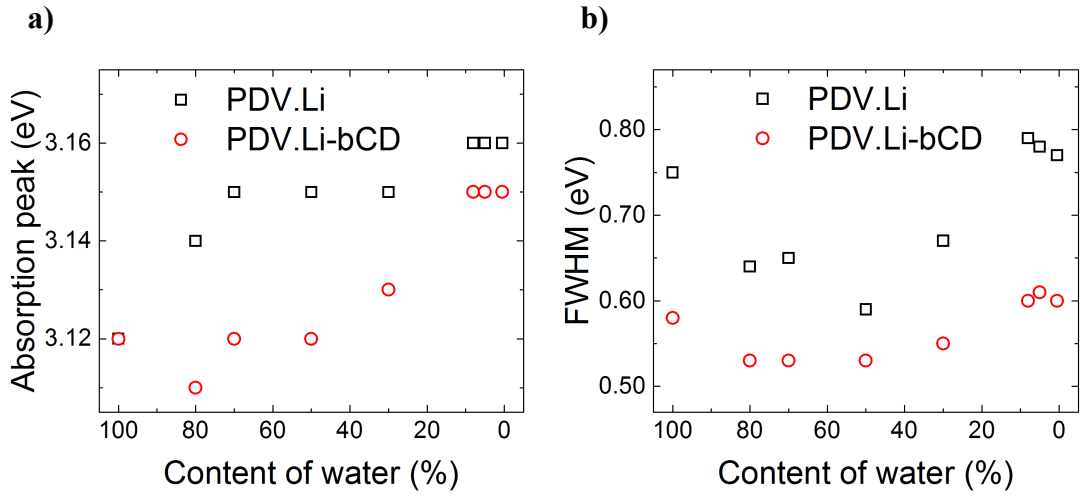

Figure S1 Absorption peak (**a**) and linewidth (**b**) for PDV.Li (black squares) and PDV.Li⊂β-CD (red circles) in water/1-propanol mixtures as a function of the water content.

c. Time-resolved photoluminescence

Figure S2

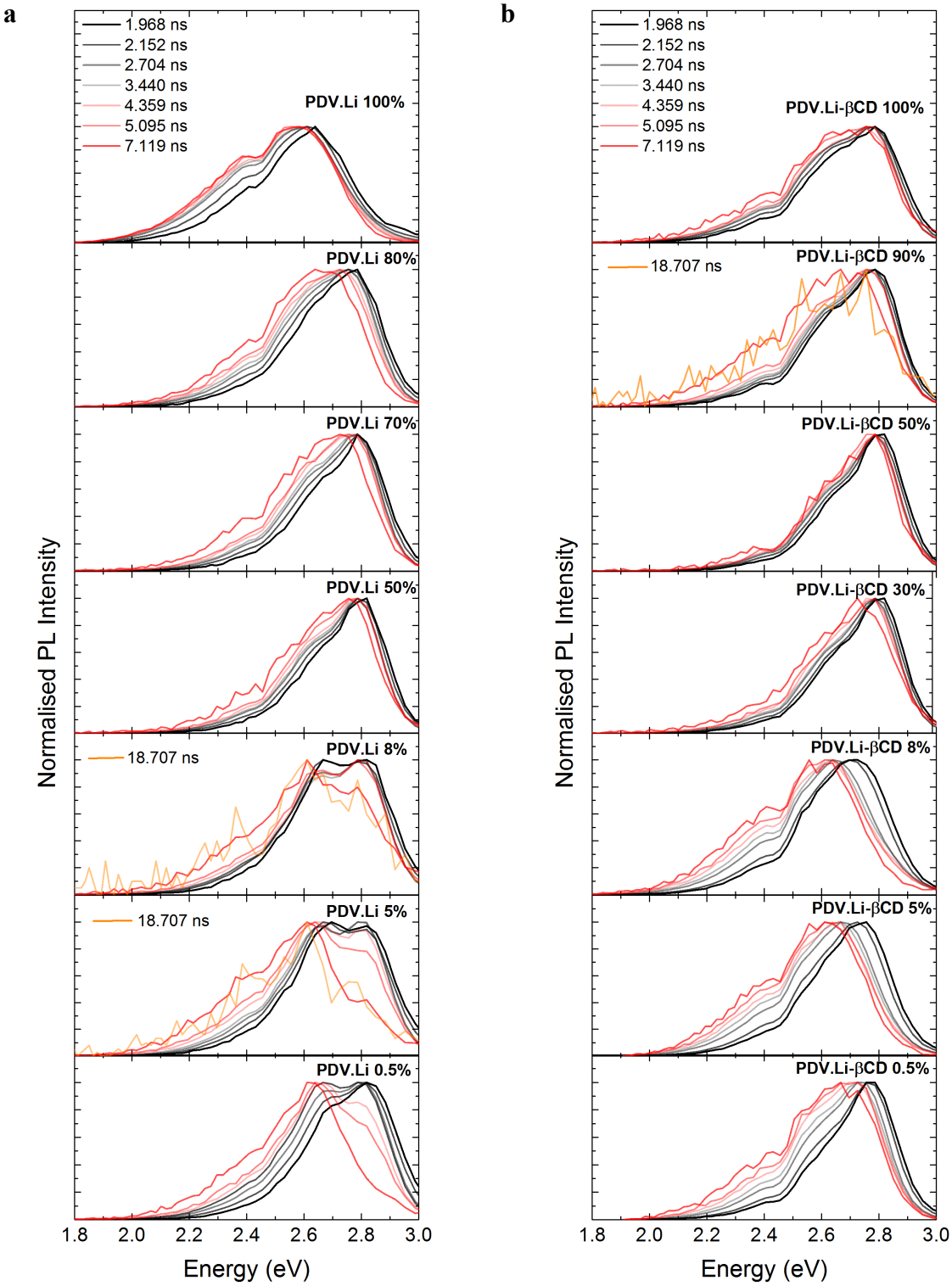

Figure S2 Normalized time-resolved emission spectra of PDV.Li (**a**) and PDV.Li⊂β-CD (**b**) aqueous solutions with increasing propanol content (% water is reported). The spectra are reported at different times after excitation.

d. Average emission energy

Figure S3

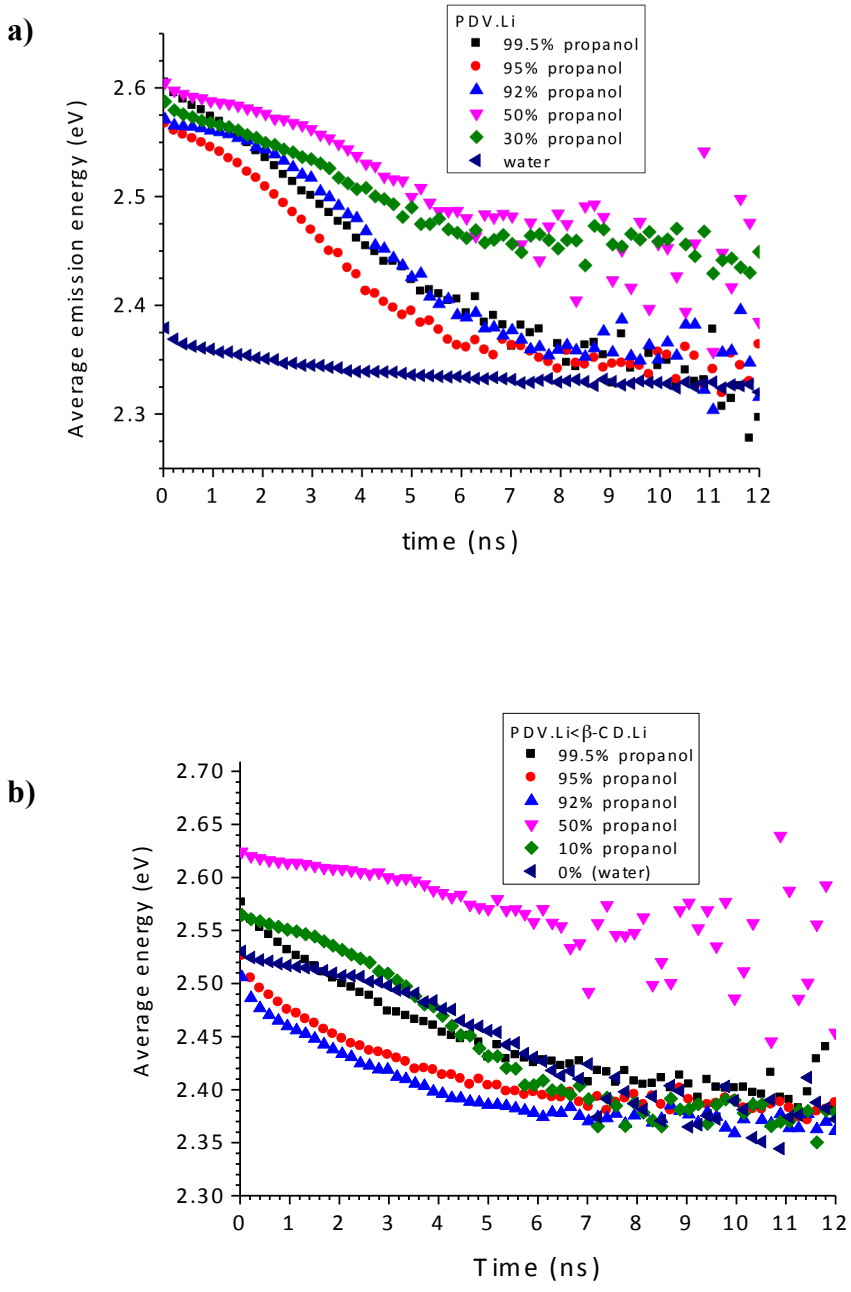

Figure S3 (**a**) Time dependence of the average emission energy in PDV.Li solutions, (**b**) Time dependence of the average emission energy in PDV.Li⊂β-CD solutions

e. Molecular modeling and simulations

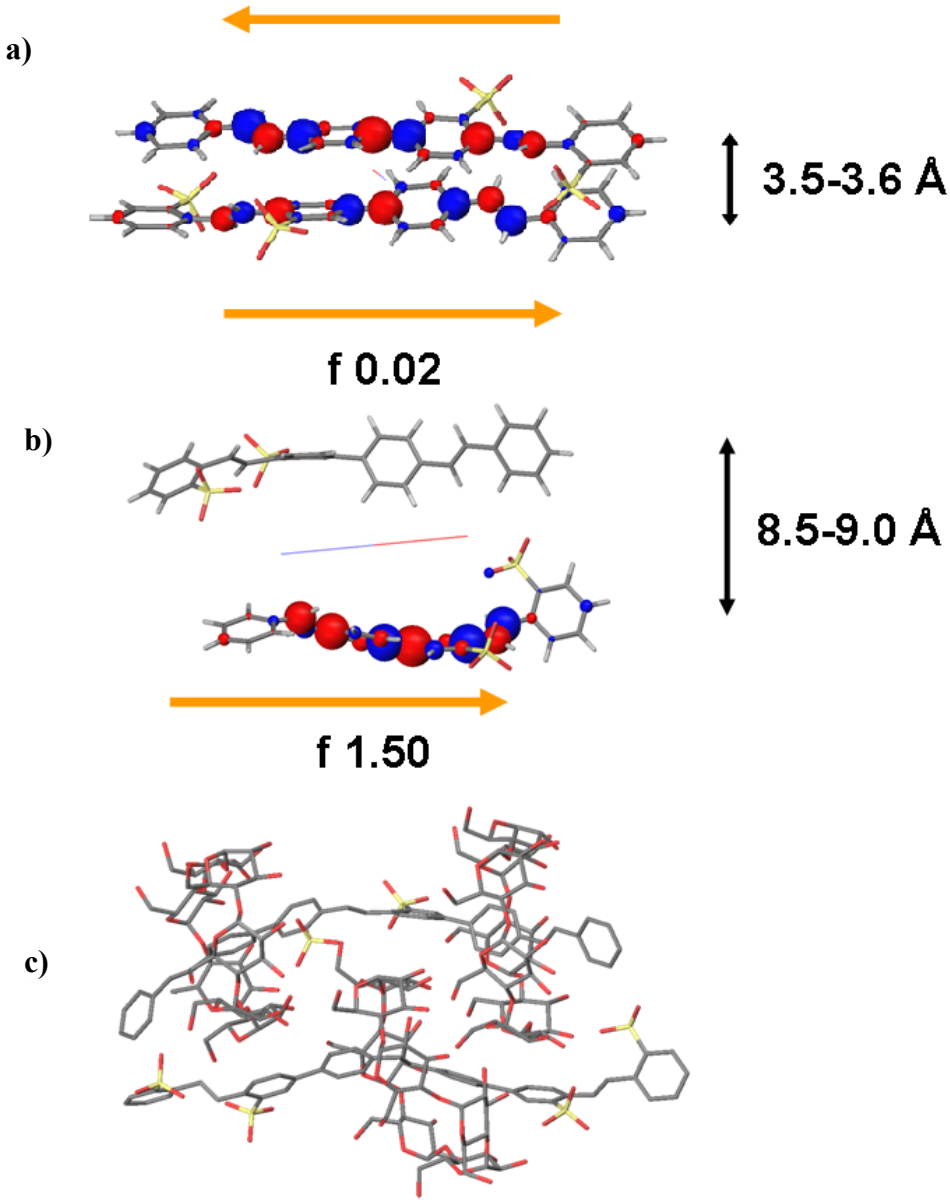

Figure S4 (**a** and **b**) Geometries of PDV.Li and PDV.Li⊂β-CD model aggregates with ZINDO/CIS atomic transition densities of the lowest excited state shown in blue and red spheres. The interchain distances are ~3.5-3.6 and 8.5-9 Å, respectively. Orange arrows indicate the direction of the net transition dipole moment of each chain. PDV.Li (**a**) shows clear H-aggregate characteristics in which transition dipole moments of individual chains cancel resulting in a low oscillator strength *f*, while those of the PDV.Li⊂β-CD (**b**) exhibit characteristics of a single chain with a high oscillator strength. In **b**, β-CD, was not included in the calculation for clarity and computational efficiency. (**c**). Geometry PDV.Li⊂β-CD model aggregate showing position of β-CD. Hydrogens have not been drawn for clarity. In all geometries, lithium ions are assumed to be dissociated, as it is likely the case in water.

The excited state calculations shown in Figure S4a and S4b were performed using ground state geometries and thus capture the extent of the lowest excited state at the time of population prior to any geometric relaxation. In the case of a symmetric cofacial stack in its ground state geometry, one would expect the lowest excited state to be delocalized across chains no matter how large the distance between them. However, for chains at large distances, the reorganization energy will exceed the strength of the interchain excitonic coupling and the exciton will self-localize onto a single chain. The fact that the lowest excited state is created as a localized intrachain exciton suggests the presence of a geometric asymmetry in the PDV.Li⊂β-CD stack.

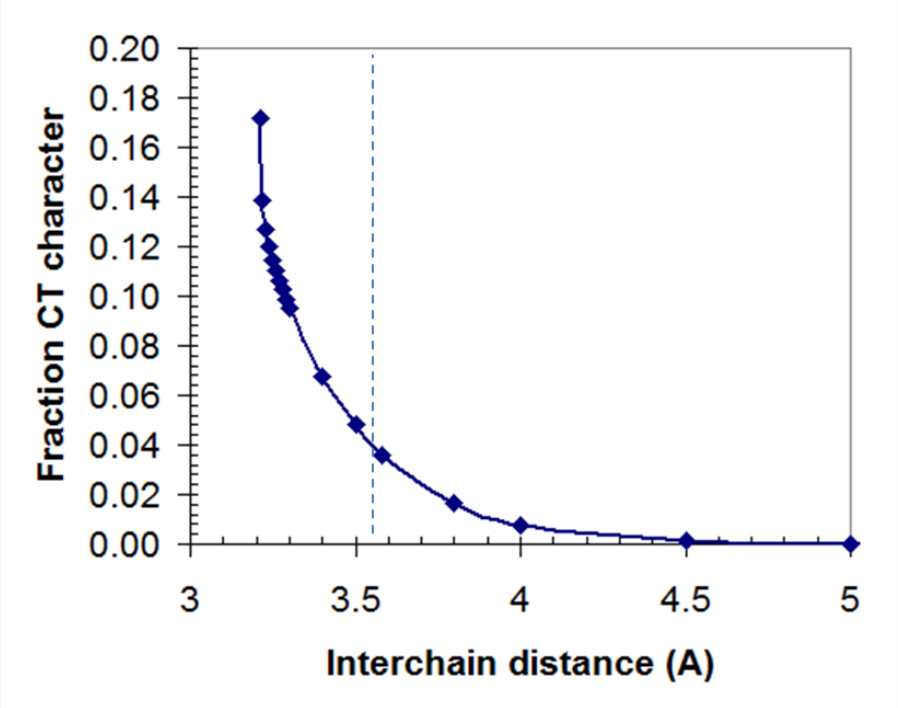

Figure S5 Plot of contribution of charge transfer configurations to the lowest excited state S1 of the model PDV.Li stack as a function of interchain displacement. The dashed line indicates the average stacking distance at the equilibrium geometry of the PDV.Li model aggregate.

References

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