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Peptide-driven charge-transfer organogels built from synergetic hydrogen bonding and pyrene-naphthalenediimide donor-acceptor interactions

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Abstract: The peptide-driven formation of charge transfer (CT) supramolecular gels featuring both directional hydrogen bonding and donor-acceptor (D-A) complexation is reported. Our design consists of the co-assembly of two dipeptide-chromophore conjugates, namely diphenylalanine (FF) dipeptide conveniently functionalized at the N-terminus with either a pyrene (Py-1, donor) or naphthalene diimide (NDI-1, acceptor). UV-Vis spectroscopy confirmed the formation of CT complexes. FT-IR and ¹H-NMR spectroscopy studies underlined the pivotal role of hydrogen bonding in the gelation process, while Electronic Paramagnetic Resonance (EPR) measurements unraveled the advantage of pre-organized CT supramolecular architectures for charge transport over solutions containing non co-assembled D and A molecular systems.

Introduction

Supramolecular chemistry and materials science are nowadays going by hand, as the first is a versatile tool for the preparation of organic functional materials with controlled structure and properties.^[1] A number of non covalent bonds have been explored for such purposes, including hydrogen bonding,^[2] electrostatic forces^[3] and donor-acceptor (D-A) interactions.^[4] Supramolecular stacks of D-A organic chromophores are being extensively studied in the field of organic electronics. The architecture of the supramolecular co-assembly determines the properties of the functional material. Segregated 1D D-A arrays have been reported to show charge-transport and photocurrent generation. They are therefore useful in optoelectronic devices. Alternate or mixed D-A arrays in which the chromophores are arranged in a face-to-face geometry and form an extended charge transfer (CT) assembly have given rise to room temperature ferroelectricity^[5] and ambipolar charge-transport.^[6] Most of these studies have been carried out on single crystals. However, the development of soft-materials with alternate D-A

supramolecular arrays has gained increasing attention in recent years.^[5c, 4, 7] In particular, gels represent a convenient alternative because of their wide applicability and ease of preparation.

The weakness and lack of directionality of the CT interaction imposes the introduction of additional non-covalent forces for the creation of CT supramolecular gels.^[4] Hydrogen bonding has been applied to select between mixed and alternate D-A stacks in supramolecular gels.^[8] By exploiting intermolecular hydrogen bonding, it was shown that the conjugation of self-assembling peptides to π -organic chromophores is a successful strategy for forming supramolecular gels with well ordered arrays of chromophores within the supramolecular architecture.^[9] A well studied self-assembling peptide motif in this field is diphenylalanine (FF). This sequence was extracted from the Alzheimer's β -amyloid polypeptides and has received great attention because of its biological relevance, chemical simplicity and excellent ability to form a wide range of nanostructures,^[10] including nanotubes^[11], nanowires^[12] and nanoarrays.^[13] Most importantly, it has proven to be extremely reliable in the formation of supramolecular gels. Lin and coworkers reported a naphthalenediimide (NDI)-FF gelator able to create one-dimensional nanostructures.^[14] Some of us recently reported a pyrene (Py)-FF conjugate that forms organogels with solvent-tuned morphologies.^[9a] Thus, the co-assembly of appropriate peptide sequences decorated with donor and/or acceptor moieties should serve as general strategy to achieve CT supramolecular gels. In this context, Ulijn and coworkers reported the biocatalytic self-assembly of NDI-dipeptide conjugates with different donors to give hydrogels.^[15] Lin *et al* described CT hydrogel formation by co-assembly of an NDI-amino acid conjugate and pyrene butyric acid.^[16] Only one of the co-assembly components was functionalized with a peptide/amino acid in these studies, hence the unfunctionalized chromophore simply intercalated in the supramolecular polymer formed by the peptide-bearing monomer. To fully exploit the self-assembly ability of peptides and expand the architectural diversity, both D and A chromophores should bear a self-assembling peptide. This approach has been recently exploited for the construction of D/A coassembled nanowires in water using ionic peptide-chromophore conjugates, though no gel formation was reported in this case.^[17] In this paper we report on our successful strategy for the realization of CT supramolecular gels from the co-assembly of D- and A-peptide conjugates. Among the many building blocks available for CT D-A interactions, we focused on the NDI-

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Riferimenti da aggiungere:

- 1) Adv. Mater. 2016, 28, 1031-1043
- 2) Acc. Chem. Res. 2011, 44, 774
- 3) Chem Commun, 2010, 46, 4267
- 4) Chem Sci, 2013, 4, 3699

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Riferimenti da aggiungere alla fine della frase, lasciando poi i riferimenti specifici che seguono nella frase successiva:

- 1) J. Am. Chem. Soc. 2009, 131, 16374-16376
- 2) Chem Commun, 2010, 46, 4285-4287
- 3) Angew. Chem. Int. Ed. 2006, 45, 5383-5386
- 4) Chem. Eur. J. 2009, 15, 388-404
- 5) Langmuir, 2010, 26 (7), pp 5232-5242
- 6) Chem. Soc. Rev., 2013, 42, 5143-5156

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pyrene pair. NDI-derivatives are superb electron acceptors due to their π -acidity,^[18] which confers under specific circumstances has been exploited to generate them a n-type semiconductors character.^[19] Moreover, their propensity to π -stacking has been extensively exploited by us and others, to obtain functional supramolecular materials.^[20] Experimental^[21] and theoretical^[22] studies indicate that the NDI-pyrene CT complex has the highest association constant among the D-A couples potentially applicable. We studied the hydrogen bond directed co-assembly of NDI- and Py-FF conjugates (**NDI-1** and **Py-1**, Chart 1) and obtained stable CT gels in a number of organic solvents, from *ortho*-dichlorobenzene (ODCB) and toluene (apolar, aromatic) to ethyl acetate and methanol (hydrogen-bond competitive, polar). Pyrene butyric acid (**2**) and compound **3** (Chart 1) were used as benchmark materials. By combining FT-IR and ¹H-NMR spectroscopies we proved that hydrogen bonding is the driving force of the gelation process. Furthermore, using Electron Paramagnetic Resonance (EPR) we investigated the photogeneration of charges within the CT gels and demonstrated that the preorganization of supramolecular architectures plays a pivotal role in the efficiency of charge transport processes.

Chart 1. Chemical structure of **Py-1**, **NDI-1**, pyrene butyric acid (**2**) and **3**.

Results and Discussion

Synthesis of the building blocks

NDI-1 was obtained by combining a microwave assisted protocol and standard solid phase peptide synthesis (details in Supplementary Information, SI). Commercially available 1,4,5,8-naphthalene-tetracarboxylic-dianhydride **4** was first condensed with decylamine to yield the corresponding naphthalenemonoimide (**5**),^[20b] and then with γ -amino butyric acid to obtain the carboxylic acid –functionalized chromophore **3** for peptide conjugation. The FF dipeptide was built on a 2-chlorotriethylchloride resin and subsequently coupled with **3**. **NDI-1** was cleaved from the resin with 1 % v/v trifluoroacetic acid (TFA) in dichloromethane (DCM) (55% yield). **Py-1** was synthesized as previously reported.^[19a]

Scheme 1. Synthesis of **NDI-1**.

Gelation ability of the individual components

We previously reported the ability of **Py-1** to gel both ODCB and acetonitrile upon sonication.^[19a] **NDI-1** formed self-supporting gels at 0.5 - 1 wt% concentrations in toluene, ODCB, ethyl acetate and methanol, while it is soluble in dimethylsulfoxide (DMSO) (Table 1 and Figure S1 of the SI). In contrast to **Py-1**, gels of **NDI-1** formed within minutes upon cooling the hot solutions to room temperature without the need of sonication. The UV-Vis spectrum of **NDI-1** in diluted DMSO solution (25 μM) showed the two characteristic vibronic bands of NDIs at 382 and 362 nm (Figures S2 and S3 of the SI). We attributed this spectral profile to the molecularly dissolved state. Broadening and appreciable bathochromic shifts of these bands were observed upon gel formation in the tested solvents (Figure S2 of the SI). Previous reports on NDI derivatives in aromatic solvents highlighted the occurrence of CT solvent-solute interactions, with absorption bands centered around 450 nm.^[23] The UV-Vis analysis of the gels of **NDI-1** in aromatic solvents ruled out the presence of such CT-interactions, as no bands were observed in that region of the visible spectrum.

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The self-assembly process was also monitored by fluorescence spectroscopy upon 359 nm excitation. The emission spectrum of **NDI-1** in the diluted DMSO solution showed one broad band centered at 434 nm with a pronounced shoulder at 550 nm. Although such emission profile did not show the mirror image of the absorption spectrum, it is in line with the generation of transient dimeric species in the excited state (excimers), which dissociate upon decaying. Congruously, the fluorescence profile was significantly altered upon gelation, with the appearance of new structureless features between 420 and 650 nm (Figure S4 of the SI). Such profile and its solvent dependency are in line with previous reports on differently functionalized self-assembling NDIs. Finally, we highlight a remarkable thermal stability for all the organogels obtained from the self-assembly of **NDI-1** as supported by the Tgel values (Table 1).

Table 1. Gelation ability of **NDI-1** in different solvents

Solvent	Result (mgc) [a]	Tgel/ °C
Toluene	G (0.5 %)	159
ODCB	G (1 %)	104
AcOEt	G (1 %)	136
MeOH	G (1 %)	102
CHCl ₃	G (1 %)	77
n-octane	I	-
DMSO	S	-

[a] G = gel, S = solution, I = insoluble, mgc = minimum gelator concentration.

CT assemblies

Next, we studied the co-assembly of **NDI-1** and **Py-1** using a 1:1 molar ratio and 1 wt% total concentration in different organic solvents. The gels were formed via the heating and cooling procedure. **NDI-1** and **Py-1** were suspended in the chosen solvent. Then, the suspensions were heated to favor solubilization and subsequently cooled to room temperature. In all cases the initial hot colorless solutions turned into red or pink gels upon cooling, pointing to the formation of a CT complex (Figure 1). Consistently, the UV-Vis spectra of the gels showed the emergence of a new band centered at around 520 nm that we assigned to the CT interaction in line with previous literature^[8d] (Figure 1). The CT band of the gels obtained at 1 wt% was more intense in toluene and ODCB compared to other solvents, suggesting a stronger CT interaction between the two chromophores in apolar solvents. In stark contrast, DMSO solutions containing both components were pale yellow: the absorption spectra showed the sum of the features of the individual components and no CT bands were observed (Figure S5 of the SI). We concluded that no self-assembly, nor co-assembly (CT interactions) occurred in DMSO.

Figure 1. Detail of the CT band region of the UV-Vis spectra of the CT gels obtained from toluene (solid line), ODCB (dashdotted line), AcOEt (dashed line) and MeOH (dotted line). Inset: photographs of the CT gels obtained from a 1:1 mixture of **NDI-1** : **Py-1** in different solvents.

The CT gels obtained were stable at room temperature and no color-changes were observed in time. Red, self-supported gels could be obtained from toluene and ODCB even at 0.5% concentration, whereas no gelation occurred in ethyl acetate and methanol at this particular concentration (Figure S6 of the SI). Finally, the photoluminescence of both D and A chromophores was quenched as a result of the CT interaction (Figure S7 of the SI).

Rheology

Responses of the CT-gels to mechanical forces were studied by strain sweep, frequency sweep and dynamic strain amplitude for gels in *ortho*-dichlorobenzene, toluene and ethyl acetate at 1% concentration. The resistance to shear deformation was assessed by frequency-sweep measurements (Figure 2a). Very similar behaviors and almost identical crossover points ($G' = G''$ at ~100 % of strain) were obtained for both ODCB and toluene. Higher strain deformations were necessary for gel failures in such apolar, aprotic solvents compared to ethyl acetate (for which, $G' = G'' < 10$ % of strain). These results suggest more robust intermolecular interactions in less-competing solvents for hydrogen bonding, as anticipated from the UV-Vis measurements. Furthermore, the impossibility of **Py-1** to gel in ethyl acetate may favor the transition from gel to liquid at lower strain deformations. Strain sweep experiments performed focused on analyzing the stiffness of such soft materials (Figure 2b). Similar rigidity was observed in all organic solvents tested (ODCB, toluene, ethyl acetate). Such measurements highlighted storage moduli well above 10^3 Pa, showing a remarkable stiffness for gels obtained from non-covalent crosslinks at this particular concentration regime. Finally, the self-recovery ability

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- 1) Chem Commun 2013, 49, 6891-6893
- 2) RSC Adv 2016, 6, 34350-34353

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of all gels was evaluated by dynamic strain amplitude experiments (Figure 2c). Alternative low and high strains (0.5% and 150%, respectively) were applied each 15 minutes, allowing to switch from linear to non-linear regime at constant angular frequency. As previously discussed for the strain sweep measurements, the polarity of the medium seemed to play a pivotal role in the kinetics of crosslink formation. A quantitative and instantaneous recovery was observed using ethyl acetate, highlighting the poor affinity of both hydrophobic peptides to polar environments. Consequently, as soon as the failure stress was released the gels were immediately reformed with almost identical stiffness. Such situation was not encountered in the two aromatic solvents, for which both peptides have a higher affinity.

Morphological studies

The rheological data were further rationalized upon studying the morphology of the self-assembled architecture with Transmission Electron Microscopy (TEM) (Figure 2d and Figure S8 of the SI). The TEM micrographs of the CT gels obtained in ODCB

highlighted the formation of an entangled network of fibers up to 5 μm in length. Fibrous structures were formed also in toluene. However, these fibers were considerably shorter than those in ODCB. The discrepancy may arise from a better solvation operated by toluene, which ultimately weakens the supramolecular architecture. The elongated fibrillar networks observed in the two aromatic solvents contrast with the flower-like structures imaged with the ethyl acetate samples. Significantly shorter, yet denser, aggregates formed in such polar solvent. The reduced extension of the CT architectures in ethyl acetate very likely explains the lower strain deformations necessary for the gel-sol transition and the much faster self-recovery ability: shorter aggregates are expected to break and reform more easily/quickly than longer ones. Finally, a mixture of fibrils and spherical structures, with a predominance of the latter, was observed in methanol. The almost total absence of entanglements in this polar and protic

Figure 2. a) Sweep strain, b) frequency sweep and c) dynamic strain amplitude experiments, performed on the CT gels obtained from ODCB (black), toluene (red), MeOH (blue) and AcOEt (green). G' full dots, G'' empty dots. d) TEM images of the CT gels obtained from ODCB, toluene, AcOEt and MeOH.

solvent accounts for the weakness of the gels therefrom originated, compared to the ones in the two aromatic solvents. Similar solvent-dependent morphologies have been observed also in the case of **Py-1**, where spherical and fiber-like aggregates formed in acetonitrile and ODCB, respectively. Other organogels reported in the literature also showed remarkable solvent-tunable morphologies. A thorough understanding of the

influence of solvent on organogels is indeed very challenging and remains one of the many open questions in the field. Hence, we can only speculate that the high hydrophobicity of the Phe-Phe dipeptide leads to the predominant formation of spherical aggregates (micelles/vesicles) upon increasing the polarity of the medium. Hydrogen bonding or D-A interactions between the spherical aggregates subsequently brings to the formation of the

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Langmuir 2009, 25(15), 8392–8394

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- 1) J. Mater. Chem., 2010, 20, 466–474
- 2) Langmuir 2010, 26(20), 16141–16149
- 3) Soft Matter, 2012, 8, 8896–8903
- 4)

gels. The shielding of the hydrophobic peptide is not encountered in less polar/apolar solvents: under these conditions the fibrillar aggregates are more favored, which ultimately results into more robust gels.

Role of hydrogen bonding and peptide secondary structure

The characterization reported so far (UV-Vis and fluorescence, rheology and morphology) shows that gelation and CT complex formation are favored in apolar aromatic solvents, whereas in polar and/or hydrogen-bonding competitive solvents both phenomena are disfavored. This behavior suggests a predominant role of hydrogen-bonding in the formation of the CT gel. Indeed, when few drops of DMSO were added to a CT gel in ODCB, a transition from red gel to transparent solution was observed within minutes. The role of hydrogen bonding in gel formation was further studied by NMR and FT-IR. The gelation process was monitored by Variable Temperature- (VT) NMR for 1 mM 1:1 **NDI-1**/**Py-1** mixtures in deuterated ODCB (ODCB-*d*₄) (Figure 3a). The ¹H NMR spectrum of the CT gel was studied in the 90°–20°C range and compared to those of the individual components (**NDI-1** and **Py-1**^[9a]) at high temperature. The sol-gel transition could be monitored by following the evolution of the amide and aromatic protons in the 6.5–5.5 and 8.5–7.5 ppm range, respectively, upon cooling (Figure 3a). In the case of the **NDI-1** component only the amide signal at 5.84 ppm could be monitored, as the other partially overlapped with the solvent signal. This peak moved to 6.03 ppm upon gel formation. For **Py-1** the amide hydrogens shifts were 0.18 and 0.12 ppm for the signals at 6.24 and 5.54 ppm, respectively. The amide shifts were accompanied by a high field shift of the aromatic protons of both NDI and pyrene cores ($\Delta\delta = 0.05$ and 0.03 ppm, respectively). Further evidence supporting the **NDI-1**/**Py-1** interdigitation were i) the more pronounced shifts of the amide protons in the co-assembly compared to those of the individual assemblies (see Figures S9 and S10 of the SI), and ii) the higher-field shift of the NDI aromatic protons, when no appreciable shift was detected in similar experiments performed with **NDI-1** alone.

The pivotal role of hydrogen bonding in the formation of the CT assemblies was further assessed with FT-IR spectroscopy (Figure 3b). The FT-IR spectra of all the gels showed a band at 3271 cm^{−1} for the NH stretching of the amide, typical of hydrogen bonded amides. The amide I region (1700 – 1600 cm^{−1}) showed a band at 1706 cm^{−1}, arising from the carboxylic group of the C-terminus and the asymmetric imide C=O stretching of the NDI, and a second band at 1660 cm^{−1} corresponding to the symmetric NDI imide C=O stretching. The third intense peak at 1639–1642 cm^{−1} arose from the amide groups of the peptide moiety. It corresponds to the classical signature of β -sheet conformation and is similar to peaks found in other diphenylalanine assemblies with β -sheet structure.^[24] Unfortunately, the partial overlap between the weak diagnostic signal of the antiparallel β -sheet (at 1680–1690 cm^{−1}) and the strong imide bands of the NDI core did not allow to distinguish the orientation of the β -sheet.

Figure 3. a) VT-NMR experiments (300 MHz, ODCB-*d*₄) performed on the CT gel. b) Detail of the FT-IR spectra of the CT gel obtained from ODCB. c) Picture of the vials containing a 1:1 **Py-1** / **3** mixture (1% wt) in different solvents. d) Picture of the vials containing the 1:1 pyrenebutyric acid / **NDI-1** mixture (1% wt) in different solvents.

To sum up, the combination of NMR and FT-IR supported that the **NDI-1**/**Py-1** co-assembly is possible thanks to a cooperative action of intermolecular hydrogen bonding and CT interaction between the electron rich pyrene and the electron-deficient NDI cores. However, it also unraveled that the main driving force of the co-assembly is hydrogen bonding. Gels featuring the CT band were not obtained when intermolecular hydrogen bonding between co-monomers was completely denied (*i.e.* in DMSO). Such hypothesis was further corroborated by co-assembly experiments of D-A pairs in which one of the components lacks the self-assembling FF dipeptide (Figure 3c and 3d). The co-assembly of a 1:1 **Py-1** / **3** mixture (1% wt) always resulted in pale red solutions, and a pale pink gel formed only in methanol (Figure 3c). On the other hand, the co-assembly of **2** and **NDI-1** led to gels in toluene and ethyl acetate (for TEM images see Figure S11 of the SI), but no CT interaction was observed (Figure 3d).

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Electron Paramagnetic Resonance (EPR) studies

Electron Paramagnetic Resonance (EPR) is often used for the photophysical characterization of photoactive materials where the photoexcitation produces stable or short-lived paramagnetic species such as free radicals, radical ions and excited triplet states.^[25] Here we applied EPR spectroscopy to identify the photogeneration of radical ions (charges) and get insights into the photophysical processes occurring in **NDI-1/Py-1** mixed systems under UV-Vis light irradiation.

We first examined room temperature EPR spectra of **NDI-1/Py-1** solutions in DMSO, where aggregation and gel formation were prevented as demonstrated in the previous sections. Before illumination with white light, the solution showed no presence of radicals. In contrast, an intense EPR spectrum was observed upon continuous sample illumination (Figure 4a). Such EPR spectrum was composed of a complex multiplet of narrow lines (0.2 gauss linewidth) and could be successfully simulated using a g-factor of 2.0030 and a set of isotropic hyperfine coupling constants deriving from the interaction of the unpaired electron with: a) two equivalent nuclei with spin $I=1$ (^{14}N), b) four equivalent ^1H nuclei and c) other four equivalent ^1H nuclei (Table 2).

Table 2. Hyperfine parameters.

Nuclei	n [a]	$ a_{\text{iso}} $ / MHz [b]
^{14}N	2	2.64
^1H	4	5.28
^1H	4	0.59

[a] n = number of equivalent nuclei, [b] a_{iso} = isotropic hyperfine coupling constant

The g-factor and hyperfine pattern are consistent with a radical having the NDI structure,^[26] leading to the assignment of the signal to the **NDI-1** radical anion. The lack of EPR spectrum in the DMSO solution of **NDI-1/Py-1** in the dark indicated that the two molecules are not capable of undergoing a thermally activated electron transfer in this solvent. The ground state of the system is therefore neutral with no charge separation, even in presence of D/A pairs. However, the electron transfer process between the two molecules was efficiently promoted under white light illumination. Stable, complete charge-separated states were revealed by the presence of the NDI radical anion.

No stable EPR spectrum was detected at room temperature in the ODCB gel even under continuous illumination. However, irradiation of a frozen ODCB gel ($T=130\text{K}$, ODCB frozen glass) resulted in an EPR spectrum similar to the one recorded in frozen DMSO under identical conditions (Figure 4c). Both EPR spectra at 130K were composed of a single unresolved line (7 Gauss linewidth), possibly resulting from a distribution of many overlapping lines. In DMSO the line shape was asymmetric,

whereas in ODCB the spectrum was almost a symmetric and homogeneous line (Lorentzian lineshape). The spectra were assigned to the radical anion of the **NDI-1** on the basis of the g-factor and spectral width coincident with the DMSO measurement at room temperature.

Figure 4. a) Black line: experimental light-on EPR spectrum of a solution of **NDI-1/Py-1** in DMSO at room temperature. Red line: best-fit simulation of the spectrum, using the hyperfine coupling constants reported in Table 2. b) The radical anion of NDI that was detected by EPR experiments. c) Normalized EPR spectra of frozen solutions of **NDI-1/Py-1** at $T=130\text{K}$, under continuous white-light illumination of the samples. d) EPR spectra decay of **NDI-1/Py-1** solutions in ODCB (green dots) or DMSO (black dots) at $T=130\text{K}$. Sample illumination is switched off at $t=0$.

The absence of the EPR spectrum at room temperature in ODCB under illumination can be explained either with a low efficiency of photoinduced electron transfer or with a very short lifetime of the photogenerated radicals. The strong intensity of the EPR spectrum detected in frozen ODCB (Figure 4c) suggests that photogeneration of charges is indeed quite efficient in this solvent. Therefore we suggest that the reason for the lack of EPR spectrum in ODCB at room temperature has to be ascribed to a very short lifetime of any photogenerated radical ion. The stronger EPR spectra observed in the DMSO solutions of **NDI-1/Py-1** are therefore caused by a much longer lifetime of the photogenerated charges in this solvent. Such hypothesis was further corroborated by the decay kinetics of the photogenerated EPR spectra measured in both DMSO and ODCB at 130K, after switching off the illumination (Figure 4d). The contrast between the two systems is striking, with radicals stable within many hours in DMSO and a decay times in the order of minutes in ODCB, indicating an efficient radical scavenging mechanism. The radicals decay is even much faster at room temperature, completely preventing their EPR detection in ODCB.

The most important radical decay process occurring in the **NDI-1/Py-1** solutions can be identified in charge recombination (back electron transfer), which restores the neutral ground-state of the two molecules. We explain the different decay rates in ODCB and DMSO on the basis of different efficiencies of charge recombination in the two solvents. In DMSO at room temperature the recombination is slow because the radical ions, after being generated, are stabilized by solvent reorganization. This causes a slow thermally activated recombination, which is even slower at low temperature due to absence of molecular diffusion. In ODCB the presence of stacked supramolecular structures allows fast charge diffusion by hopping along the stacks, which ultimately increases the probability of collisions and charge recombination both at low and high temperature. The EPR lineshapes at low temperature provided further support to this explanation (Figure 4c). The lorentzian EPR lineshape in ODCB results from an almost complete averaging of anisotropies due to fast motional averaging, whereas the EPR spectrum in DMSO maintains the asymmetric lineshape caused by the g-factor anisotropy that cannot be averaged because of the negligible electron hopping among the solvent-separated molecules.

Conclusions

In conclusion, we have reported our strategy for the realization of CT supramolecular gels in a variety of organic solvents. The peculiar feature of our design resides in the co-assembly of a self-assembling diphenylalanine peptide functionalized with either a naphthalenediimide- (**NDI-1**) or a pyrene (**Py-1**) moiety. The occurrence of the donor-acceptor (D-A) interaction in the co-assembly was phenomenologically observed by the formation of red organogels, and was further assessed through the CT-band around 520 nm in the UV-Vis spectra and the quenching of the fluorescence of both NDI and Py chromophores. Rheology measurements performed on the CT gels highlighted an enhanced robustness in the aromatic solvents due to a lack of competition for hydrogen bonding. This is coherent with the morphological studies performed by TEM: elongated fibrillar networks were visualized in toluene and ODCB. The higher robustness in the aromatic solvents is counterbalanced by a much quicker self-recovery ability in polar and hydrogen-bond competing ethyl acetate. The less elongated structures visualized by TEM in this particular solvent, coherently point to aggregates that can be disrupted and regenerated more dynamically. The key role played by hydrogen bonding in the co-assemblies was further underlined by NMR and FT-IR spectroscopies. The pivotal role of hydrogen bonding in the gelation process was finally assessed by additional co-assembly experiments where one of the components was lacking the FF motif: both gelation ability and CT complex formation were negatively affected. Finally, EPR measurements showed that the preorganization of the supramolecular stacks in ODCB gels allows for a very efficient charge recombination, explainable as an effect of the fast charge diffusion, highly favoured by hopping along the D-A arrays. This highlights the

high potential of alternate D-A stacks as charge-transport systems.

Experimental Section

General Methods.

Solvents and reagents. Solvents were of analytical reagent grade, laboratory reagent grade, HPLC grade or anhydrous. All other reagents were used as received. **NMR.** ^1H , ^{13}C and 2D NMR were recorded at 289 K on a Bruker Avance 300, Bruker Avance III 500 and Bruker Avance DPX 600 instruments using the partially deuterated solvent as internal reference. The multiplicity of a signal is indicated as: s – singlet, d – doublet, t – triplet, m – multiplet, dd – doublet of doublets, etc. **FT-IR.** FT-IR Spectra were recorded with a Nicolet 5700 FT-IR spectrophotometer, and a Perkin Elmer Spectrum One 1600 FT-IR spectrometer, equipped with a Perkin Elmer Universal ATR Sampler Accessory, at a nominal resolution of 2 cm^{-1} , averaging 100 scans. **The measurements were performed on compounds as powders, whereas the organogels were dried under a flow of N_2 and subsequently measured.** **Mass Spectrometry.** ESI-MS experiments were performed in a ESI-TOF Mariner™ Biospectrometry™ Workstation of Applied Biosystems by flow injection analysis using acetonitrile with formic acid (1%) as mobile phase. **MALDI-TOF-MS** were obtained using α -Cyano- 4-hydroxycinnamic acid (CHCA) and trans-2-[3-(4-tert-Butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB) as matrices on a PerSeptive Biosystems Voyager-DE PRO spectrometer. **HPLC.** The HPLC measurements were performed using an Agilent 1200 series apparatus (Palo Alto, CA), equipped with a UV detector at 226 nm. The working conditions used were: Kromasil C18 100 A (stationary phase), 30–100% B, 20 min, 1 mL/min (eluent: A= 9:1 $\text{H}_2\text{O}/\text{CH}_3\text{CN}$, 0.05% TFA; B= 1:9 $\text{H}_2\text{O}/\text{CH}_3\text{CN}$, 0.05% TFA). **UV-Vis Absorption.** UV-Vis absorption spectra were recorded using a Varian Cary 100 spectrophotometer. A 1 cm path length quartz cell was used. **Emission spectroscopy.** Fluorescence spectra were recorded on a Perkin-Elmer model LS-50B or a CaryEclipse fluorescence spectrophotometer. **Transmission electron microscopy.** TEM images were registered on a Jeol 300PX instrument. A glow discharged carbon coated grid was floated on a small drop of solution and excess was removed by #50 hardened Whatman filter paper. Samples of the gels were prepared by dropping a small amount of gel into a glow discharged carbon coated grid and removing excess of gel with #50 hardened Whatman filter paper. **Rheology.** Samples were prepared according to the gel formulation on a total 400 μL volume and they were immediately transferred onto the plate. An anti-evaporation chamber was used during the measurements to prevent the drying of the gels. All measurements were performed at 25 $^\circ\text{C}$ and they were done subsequently following this order: angular frequency, strain sweep and dynamic strain amplitude. Time sweep and angular frequency measurements were performed at 0.5 % strain amplitude (linear regime). Strain sweep measurements were performed at 10 rad/s angular frequency. Dynamic strain amplitude measurements (gel recovery) were performed at alternatively 0.5 % (linear regime) / 150 % (nonlinear regime which induced gel network failure for all gels) strain amplitudes each 15 min and at constant 10 rad/s angular frequency. **Electron Paramagnetic Resonance.** EPR measurements were performed on an X-band (9.6 GHz) ER200D Bruker spectrometer, equipped with a nitrogen-flow variable temperature system (Bruker BVT2000), for sample temperatures control from 130 K to 300K. To obtain light-induced EPR spectra, the source of white-light illumination of the samples was a 300W Xe lamp, IR filtered and focused into a quartz optical fiber bringing the light to the sample inside the cavity of the EPR spectrometer. EPR spectral simulations were performed using Easyspin, a Matlab™ toolbox.^[27] For EPR experiments, mixed solutions of PB-FF/NDI-FF (7 mM each) in ODCB and in DMSO were inserted into EPR quartz tubes

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Commented [BJ10]: In risposta al punto 6 del referee 1. Qui ti incollo quello che ha scritto Silvia nella mail: UV-Vis: spettri registrati direttamente sul gel. Rileggendo la parte sperimentale del manoscritto mi sono accorta che abbiamo messo di aver utilizzato la cella con cammino ottico da 1 cm invece abbiamo usato quella apribile da 0.2 mm.

Emissione: campioni preparati analogamente a quelli per le misure UV-Vis e la cella usata era una a volume ridotto con cammino ottico da 1cm. Per quanto riguarda i parametri strumentali ho provato a guardare se nei file txt delle misure ci fossero tutte le info. C'è una serie di numeri prima dei dati ma non sono riconducibili ai parametri strumentali. Forse dovremmo ricontrollare direttamente dallo strumento.

and subsequently sealed off after several freeze-pump-thaw cycles, to eliminate dissolved oxygen which affects the photogeneration and lifetime of excited states and of radicals.

Preparation of gels. The gels were prepared by weighing a calculated amount of NDI-FF and/or PB-FF in a vial equipped with a sealed teflon cap. A calculated volume of solvent was then added to the dry powder to reach a final 1wt% concentration. The obtained mixture was subsequently heated up to get a clear solution and then slowly cooled down to room temperature. Gelation occurred during cooling.

Synthesis of 3. The reaction was repeated 7 times on a 1 gram scale. 1,4,5,8-naphthalene-tetracarboxylic-dianhydride (1 g) was weighed in a 20 mL microwave vial and DMF (10 mL) and decylamine (0.745 mL) were added. The mixture was sonicated for 2-3 minutes and then sealed. The reaction mixture was heated for 5 minutes at 140 °C and then cooled to room temperature, where a gel-like material formed. The gel-like material was broken with a spatula and poured into 150 mL of basic water (pH $\geq$ 10) where a first precipitate was obtained (symmetric bis(C₁₀)NDI). The solid was filtered and washed with neutral water. The basic water solution was then acidified to pH 5 and a second precipitation occurred. Filtration of this suspension afforded the desired naphthalenemonoimide C₁₀NMI (**5**) (white solid, 4.79 g, 45% yield) whose spectra data agree with those previously reported.^[20b] Compound **5** (4.36 g) was introduced into a 100 mL round bottom flask and γ -amino butyric acid (3.34 g), DIPEA (5.9 mL) and DMF (50 mL) were added. The reaction mixture was stirred at 90 °C overnight. The reaction mixture was poured into water (350 mL) and the pH adjusted to 3 by addition of 6M HCl, which caused precipitation. The precipitated **3** was filtered, washed with water and dried (off yellow powder, 1.73 g, 33% yield). **¹H-NMR:** (400 MHz, DMSO-*d*₆) δ : 8.65 (s, 4H), 4.10 (t, J = 8Hz, 2H), 4.04 (t, J = 8Hz, 2H), 2.33 (t, J = 8Hz, 2H), 1.93 (p, t, J = 8Hz, 2H), 1.65 (p, J = 8Hz, 2H), 1.37-1.22 (m, 12 H), 0.84 (t, J = 8Hz, 3H). **¹³C NMR** (100 MHz, CF₃CO₂D) δ : 167.32, 134.52, 134.48, 128.98, 128.91, 128.85, 128.74, 128.56, 44.33, 42.80, 33.77, 33.01, 31.35, 31.33, 31.15, 31.07, 29.66, 28.79, 24.49, 24.36, 14.65. **FT-IR (ATR)** ν (cm⁻¹): 2922, 2848, 1703, 1655, 1581, 1455, 1375, 1333, 1247, 890, 768, 564. **MALDI-TOF-MS** for C₂₈H₃₂N₂O₆ calculated 492.23 g/mol, measured m/z = 492.25 [M]⁺.

Synthesis of NDI-1. NDI-1 was synthesized using standard solid phase 9-fluorenylmethoxycarbonyl (Fmoc) chemistry (see SI for more detail). The 2-chlorotriptyl resin was used (commercial loading 1.63 mmol/g). For deprotection of the Fmoc group a 20% solution of piperidine in DMF was used. For attachment of the first amino acid the resin was treated with a solution of the corresponding amino acid and diisopropylethylamine in dichloromethane. For each coupling a mixture of *O*-(Benzotriazol-1-yl)-*N,N,N'*,*N'*-tetramethyluronium hexafluorophosphate (HBTU), 1-Hydroxybenzotriazole hydrate (HOBt) and *N,N*-Diisopropylethylamine in DMF was used to activate the carboxylic acid. Final cleavage was performed using a 5% solution of trifluoroacetic acid in dichloromethane. A glass reactor for solid phase peptide synthesis was employed and, when not in use, the resin was dried and stored in the freezer with the amino-terminus Fmoc-protected. Before each step, the resin was pre-swelled with 10 mL/g of DMF (1 x 20 min). NDI-1 was obtained from 450 mg of resin as a pale brownish solid (433 mg, 57%) **¹H-NMR:** δ_{H} (300 MHz; dmsO-*d*₆) 12.70 (s, 1H, OH), 8.65 (s, 4H, Ar), 8.18-8.16 (d, 1H, NH), 7.98-7.95 (d, 1H, NH), 7.24-7.19 (m, 10H, Ar), 4.50-4.41 (m, 1H, α -CH), 4.06-3.99 (m, 1H, α -CH), 3.07-2.86 (m, 4H), 2.73-2.60 (m, 4H), 2.14-2.10 (t, 2H), 1.77-1.65 (m, 4H), 1.32-1.24 (m, 14H, aliphatic), 0.84 (t, 3H, CH₃). **¹³C-NMR:** δ_{C} (25 MHz; dmsO-*d*₆) 174.57, 173.21, 164.52, 164.48, 139.84, 139.31, 132.33, 131.05, 130.08, 129.85, 128.32, 128.22, 128.16, 128.04, 55.39, 55.32, 39.36, 38.57, 34.85, 33.21, 30.88, 30.83, 30.66, 30.62, 29.29, 28.43, 25.66, 24.03, 15.89. **FT-IR (KBr):** ν (cm⁻¹) 3282, 3062, 3030, 2924, 2853, 1706, 1662,

1582, 1542, 1496, 1455, 1377, 1340, 1245, 1197, 1165, 1121, 1092, 1051, 1030, 961, 920, 880, 769, 747, 700, 564. **ESI-MS:** m/z = 787.5 [M+H]⁺

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Keywords: gels • charge transfer • peptides • self-assembly • EPR

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Title

Layout 2:

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Dr. Silvia Bartocci, Dr. Jose Augusto Berrocal, Paola Guarracino, Prof. Dr. Lorenzo Franco and Prof. Dr. Miriam Mba*

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Title

Charge transfer supramolecular gels were obtained from dipeptide donor-and acceptor conjugates. The presence of the peptide segment in both the donor and acceptor components was necessary for the formation of the charge transfer gels. EPR demonstrated that the preorganization of the supramolecular stacks in the gels leads to very efficient charge recombination.