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How to cite

BOLAG, Alatengbaolige, SAKAI, Naomi, MATILE, Stefan. Dipolar Photosystems: Engineering Oriented Push-Pull Components into Double- and Triple-Channel Surface Architectures. In: Chemistry, 2016, vol. 22, n° 26, p. 9006–9014. doi: 10.1002/chem.201600213

This publication URL: https://archive-ouverte.unige.ch/unige:84653
Publication DOI: 10.1002/chem.201600213

ChemPubSoc Europe
DOI: 10.1002/chem.201xxxxxx
CHEMISTRY
A European Journal
Full Paper

Supramolecular Chemistry

Dipolar Photosystems: Engineering Oriented Push-Pull Components into Double- and Triple-Channel Surface Architectures

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Abstract: Push-pull aromatics are not popular as optoelectronic materials because their supramolecular organization is difficult to control. However, recent progress with synthetic methods suggested that the directional integration of push-pull components into multicomponent photosystems should become possible. In this study, we report the design, synthesis and evaluation of double- or triple-channel architectures that contain π stacks with push-pull components in parallel or mixed orientation. Moreover, the parallel push-pull stacks were uniformly oriented with regard to co-axial stacks, either with inward or outward oriented push-pull dipoles. Hole-transporting (p) aminoperylenemonoimides (APIs) and aminonaphthalimides (ANIs) are explored for ordered push-pull stacks. For the co-axial electron-transporting (n) stacks, naphthalenediimides (NDIs) are used. In double-channel photosystems, mixed push-pull stacks are overall less active than parallel push-pull stacks. The orientation of the parallel push-pull stacks with regard to the co-axial NDI stacks has little influence on activity. In triple-channel photosystems, outward directed dipoles in bridging stacks between peripheral p and central n channels show higher activity than inward directed dipolar stacks. Higher activities in response to direct irradiation of outward-directed parallel stacks reveals the occurrence of quite remarkable optical gating.

Introduction

Dipolar, or push-pull chromophores are characterized by red-shifted absorption and highly polarized excited state.[1-4] These properties are fully exploited in some of the most efficient dye-sensitized solar cells.[2] Their use in other types of organic optoelectronics is limited because of their tendency to cause disorder. However, recent studies have shown the potential of dipolar aromatics to achieve high performance optoelectronics depending on their long-range molecular order.[1] Push-pull compounds intrinsically prefer to form antiparallel π stacks by dipole-dipole attraction. The alternative parallel stacks with uniformly oriented push-pull dipoles would generate quite significant dipolar fields. Although dipoles have been shown to influence the rate of electron transfer in solutions and in self-assembled monolayers,[5] the applicability of such effects to more complex systems is quite poorly explored, mostly because the synthesis of the required multicomponent architectures has been impossible so far.

Recently, we became interested in the development of general synthetic strategies to build multicomponent surface architectures with controlled and variable organization. Among several methods we developed,[6] self-organizing surface-initiated polymerization (SOSIP) turned out to be the most versatile. Synthetic access to multicomponent architectures of increasing complexity has been secured with the addition of templated stack exchange (TSE).[8] This SOSIP-TSE methodology has allowed us to build triple-channel photosystems,[9] double-channel[10] photosystems with antiparallel redox gradients in both channels (OMARG-SHJs),[11] and ion-gated photosystems.[12] In this report, SOSIP-TSE is used to elaborate on dipolar photosystems.

Amino[3]-perylenemonoimides[13] (APIs) were selected first as push-pull component in dipolar stacks because their close relatives, perylenediimides (PDIs) perform particularly well in double-channel SOSIP-TSE photosystems. Contrary to common assumptions in the literature, PDIs in combination with the classical naphthalenediimides (NDIs)[14] act as excellent p transporters.[15] Efficient charge separation between perylenemonoimides and NDIs has also been well established.[3a,13b] Most importantly, covalent face-to-face API dimers has been shown to undergo symmetry breaking charge separation.[3b] This process was identified as important to achieve efficient interchannel charge separation in SOSIP.[16] As far as fundamental properties are concerned, APIs excel with

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strong absorbance in the visible range, HOMO-LUMO energy levels that are compatible with NDIs as n transporters, and strong dipole moments in the ground (~5 D) and the S_1 excited state (~20 D).[3]

Smaller homologs of APIs, aminonaphthalimides (ANIs)[4][17] retain most of the favorable properties described above with a larger band gap. They were thus included in this study as alternative push-pull component. ANIs are well-known for their preference to accept electrons from the donor side.[4b,c] This directionality has been of interest for the construction of multistep electron-transfer chains.[4d,e]

In this report, parallel and antiparallel APIs and ANIs are engineered into SOSIP-TSE architectures to generate oriented supramolecular dipolar fields. Coupled with co-axial electron-transporting channels in double-channel photosystems, we find that the orientation of parallel stacks does not significantly affect the photocurrent generation, whereas uncontrolled or antiparallel orientations give poorer activities. Installed as a bridge in triple-channel photosystems, oriented dipolar stacks more significantly affect photoactivity, particularly when directly irradiated.

Results and Discussion

Design. In the envisioned dipolar double-channel photosystems, one of the two charge-transporting π stacks is composed of push-pull aromatics. The intrinsically favored antiparallel stacking results in mixed stacks without supramolecular dipolar fields (Figure 1b). The intrinsically disfavored parallel stacks of push-pull aromatics have an extended supramolecular dipolar field (Figures 1a and c). Rather rich in electrons, push-pull stacks are likely to act as hole-transporting (p) channels. In double-channel photosystems, parallel push-pull stacks are thus aligned next to electron-transporting (n) channels. Parallel push-pull stacks can align along n-transporting channels in two orientations. Parallel push-pull stacks with positive ends of dipole moments near the n-transporting partner are referred to as *outward* dipolar photosystems (Figure 1a). The complementary *inward* photosystems have their negative ends near the n-transporting channel (Figure 1c). These dipolar double-channel photosystems could so far not be explored experimentally because synthetic methods for their construction were not available.

The recently introduced SOSIP-TSE methodology[7,8] offers all that is needed to construct *outward* and *inward* dipolar double-channel photosystems as well as their mixed controls (Figure 1). Namely, SOSIP uses ring-opening disulfide-exchange polymerization[18] under mildly basic conditions to grow n-transporting π stacks directly on solid oxide surfaces (Figure 2). In TSE, the orthogonal[19] dynamic-covalent hydrazone exchange[20] under mildly acidic conditions is then used to grow a second π stack along the original stack obtained by SOSIP. The directionality of hydrazone exchange promised synthetic access to dipolar architectures by SOSIP-TSE methodology. Namely, push-pull chromophores with an aldehyde at the donor side should give *outward* dipolar architectures such as photosystem ***out*-1** (Figure 2). Push-pull chromophores with an aldehyde at the acceptor side should give the complementary *inward* dipolar architectures ***in*-1**. Co-TSE with both aldehydes at the same time should give architectures ***mixed*-1** without strong supramolecular dipolar fields.

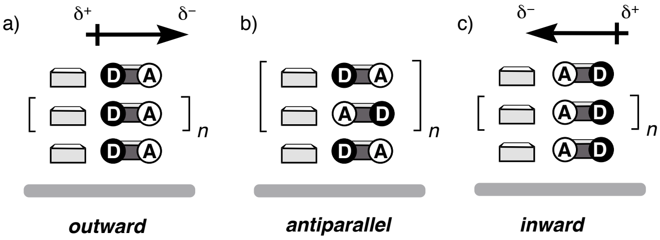


Figure 1. Definition of antiparallel (b) as well as *outward* (a) and *inward* (c) dipolar double-channel architectures.

Monomer Synthesis. API **2** was designed as target molecule for the construction of the *outward* dipolar photosystem ***out*-1**, and API **3** was developed for ***in*-1** (Scheme 1). Both target molecules were synthesized from perylenedianhydride **4**. Following literature procedures,[3,13] the bulky amine **5** was used as a temporary solubilizer to facilitate the preparation of monoimide **6** under harsh conditions. From there, bromination gave monoimide **7**, which was hydrolyzed to give anhydride **8** as a common key intermediate for the synthesis of both API **2** and API **3**.

For API **2**, anhydride **8** was first reacted with the previously reported[9a] solubilizing leucine derivative **9**. The obtained imide **10** was then subjected to nucleophilic aromatic substitution with piperazine (**11**) to give push-pull API **12**, which in turn was coupled with aldehyde **13** by routine amide bond formation. API **3** was prepared analogously. Namely, anhydride **8** was first reacted with amine **14**. Reaction of the obtained imide **15** with amine **11** gave API **16**, which was elongated with the leucine solubilizer **17** and finally equipped with aldehyde **13**.

The ANI aldehydes **18** and **19** were prepared similarly from commercially available 4-bromo-1,8-naphthalic anhydride. The details can be found in the supporting information.

Monomer Characterization. The optoelectronic properties of monomeric APIs were confirmed to be as expected.[3] Namely, cyclic voltammetry (CV) and differential pulse voltammetry (DPV) measurements afforded the HOMO and LUMO energy levels in CH_2Cl_2 (Figure 3a). The found values were consistent with the literature and compatible with electron transfer from excited APIs to NDIs and hole transfer from excited NDIs to APIs.

In absorption and emission spectra of all prepared APIs, the positive solvatochromism characteristic for push-pull fluorophores,[21] including ANIs,[17] was fully confirmed (Figure 3c).[3a,h] The emission band originates presumably from a twisted intramolecular charge transfer (TICT) state, typical for disubstituted amino donor groups.[21d] The absorption maximum in BMI (1 butyl-3-methylimidazolium acetate), an ionic liquid, was much more red shifted than expected from the rather low dielectric constant (ε ~ 15).[22] The λ_{max} = 536 nm appeared clearly beyond the λ_{max} = 526 nm in acetonitrile or λ_{max} = 531 nm in DMF (ε ~ 37), even slightly beyond the λ_{max} = 534 nm in DMSO (ε ~ 47). This red-shifted absorption in ionic liquids could originate from complex **20** with the recently described ionpair-π interactions[17] operating from both sides. Considering that red-shifted absorption has been noticed for several push-pull

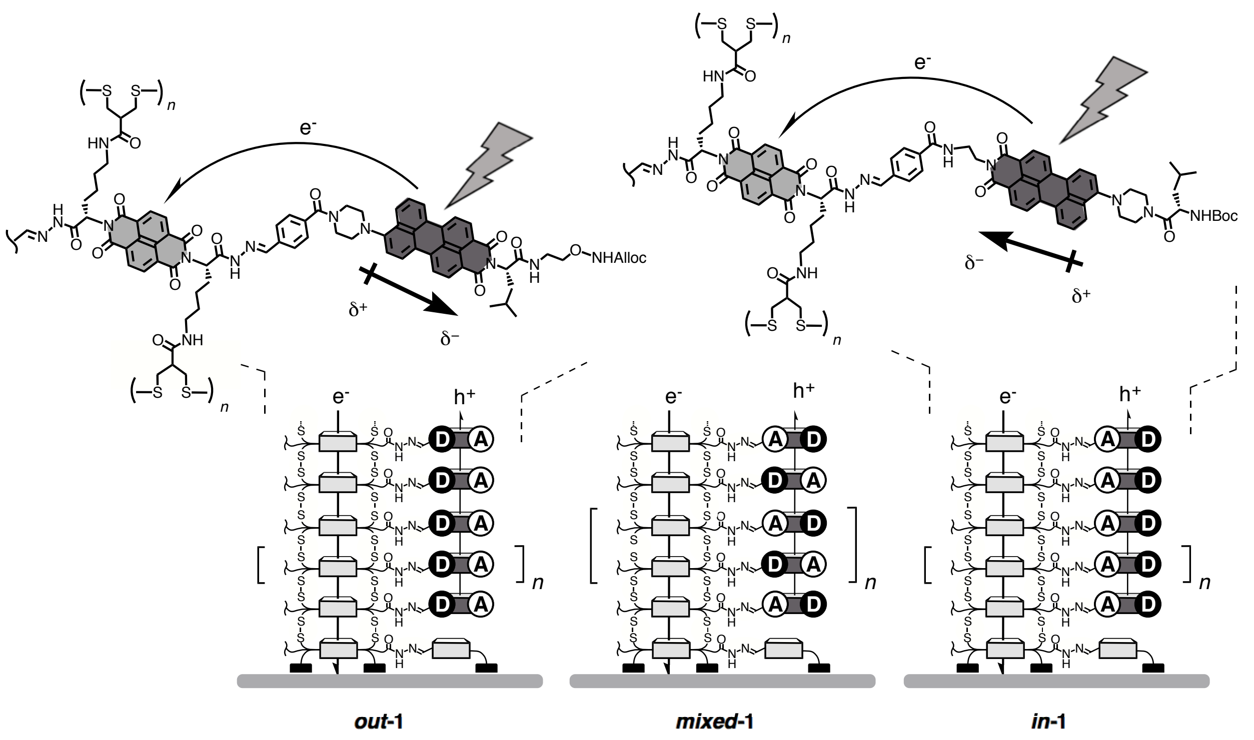
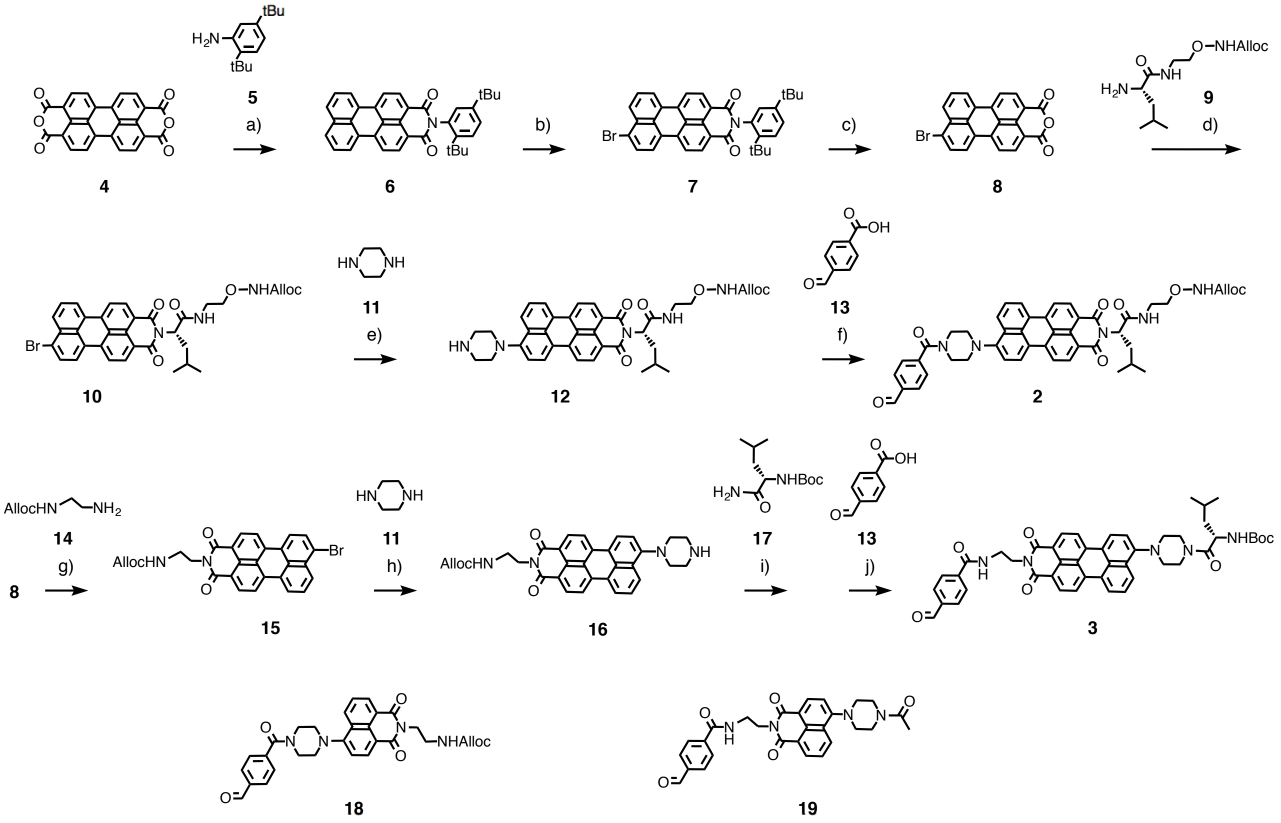


Figure 2. Schematic, idealized structures of dipolar double-channel architectures with the supramolecular dipolar field in the parallel API stack pointing away from and toward the NDI stack in photosystems ***out*-1** and ***in*-1**, respectively, together with macrodipole-free photosystem ***mixed*-1**. The corresponding ANI photosystems are designated as ***out*-1N**, ***in*-1N** and ***mixed*-1N**, respectively.



Scheme 1. a) $Zn(OAc)_2 \cdot H_2O$, imidazole, H_2O, microwave, 190 °C, 30 min, 70%;[17e] b) Br_2, PhCl, 50 ºC, 16 h, 92%; c) 1. KOH, *t*-BuOH, reflux, 15 h; 2. AcOH, rt, 2 h, 79% (2 steps); d) $Zn(OAc)_2 \cdot H_2O$, imidazole, 100 °C, 2 h, 80%; e) TEA, DMF, 90 ºC, 18 h, 59%; f) HBTU, TEA, DMF, rt, 30 min, 52%; g) $Zn(OAc)_2 \cdot H_2O$, imidazole, 100 °C, 2 h, 75%; h) TEA, NMP, 90 ºC, 18 h, 81%; i) HBTU, TEA, DMF, rt, 30 min, 51%; j) 1. $Pd(PPh_3)_2Cl_2$, $n Bu_3SnH$, AcOH, CH_2Cl_2, rt, 30 min; 2. HBTU, TEA, DMF, rt, 30 min, 65% (2 steps).

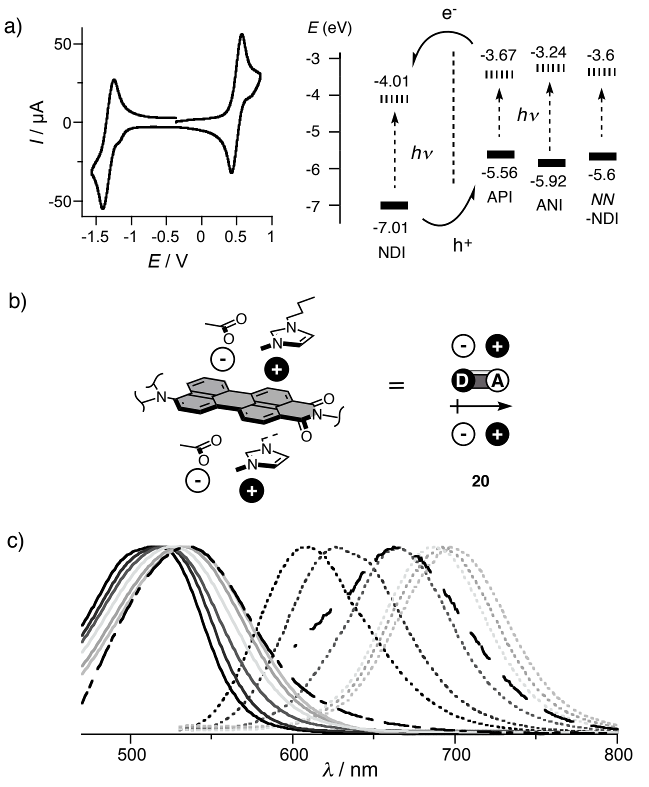
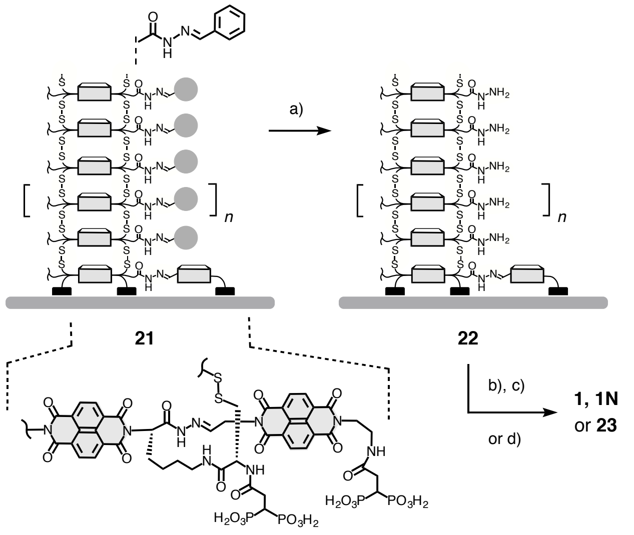


Figure 3. a) Cyclic voltammogram of API **2** in CH_2Cl_2, and HOMO (bold) and LUMO (dashed) energy levels against vacuum, relative to -5.1 eV for Fc^+/Fc, compared to reported values for NDIs and ANIs. b) Schematic structure of the notional ionpair-π complex **20** between API **2** and BMI. c) Normalized absorption (left) and emission spectra (right) of **2** (absorption, left to right: CCl_4 (ε = 2), toluene (ε = 2), THF (ε = 8), MeCN (ε = 38), DMF (ε = 37), DMSO (ε = 47), BMI (ε ~ 15)[22]; emission, left to right: CCl_4, toluene, THF, BMI, MeCN, DMF, DMSO).

chromophores in ionic liquids,[23] we conclude that ionpair-π interactions could be much more common and functionally much more important than expected so far.

Photosystem Synthesis. Dipolar photosystems were prepared from the previously reported SOSIP surface architecture **21** (Scheme 2).[8,9] As described elsewhere in much detail, initiators composed of a central NDI, two protected thiols in the main chain and two peripheral NDI templates in the side chain were attached on indium tin oxide (ITO) surfaces *via* four diphosphonate bonds. After the formation of monolayers of initiators on ITO, the thiols were deprotected and deprotonated to initiate the ring-opening disulfide-exchange polymerization of the propagators from the surface. These propagators contain a NDI to afford oriented stacks on the central NDIs of the initiators, strained disulfides above the thiol initiators to produce poly(disulfide)s along the central NDI stacks, and hydrazides protected with benzaldehyde templates. The resulting SOSIP surface architectures such as **21** have been characterized previously in much detail with regard to directional growth from the surface (microcontact printing), surface roughness (below that of the underlying ITO surface), long-range organization down to the molecular level (phase-contrast AFM), self-repair of errors during polymerization, and so on.[7-9] In the API series, SOSIP films with an NDI absorbance at 385 nm of roughly 0.5 were used (Figure 4). This corresponds to the surface architecture **21** with stacks of *n* ~ 500 NDIs and a height of ~ 180 nm (Scheme 2).

The benzaldehyde templates along the central NDI stack of **21** were removed first with excess hydroxylamine.[8,9] The hydrazides liberated along the NDI stacks in **22** were then reacted with aldehydes **2** and **3**. For *outward* dipolar photosystem ***out*-1**, electrodes **22** were incubated in 25 mM solutions of API **2** in DMSO/AcOH 10:1 at 40 ºC. The increase of API absorption band demonstrated its incorporation in the photosystem (Figure 4a). Comparison of the NDI and the API absorbance provided a qualitative estimation of the TSE yield for the synthesis of photosystem ***out*-1**. Maximal observed TSE yields were 79% with API **2**. The complementary photosystem ***in*-1** was obtained in ≤ 69% by incubating electrode **22** in a solution of API **3**. Co-TSE of electrode **22** in equimolar solutions of API **2** and API **3** gave the ***mixed*-1** in ≤ 69% yield. Considering the large size of the API stack exchangers compared to the NDI templates on the surface, these yields were within expectations for the formation of tightly packed, organized stacks. Without hydrazone formation, stack exchangers are not bound to the surface architectures. This dynamic covalent interfacing by hydrazone formation assures that the orientation of the push-pull APIs relative to the central NDI stack is as drawn in *outward* dipolar photosystem ***out*-1**, *inward* dipolar photosystem ***in*-1** and photosystem ***mixed*-1** (Figure 2).



Scheme 2. a) NH_2OH, H_2O, pH 5, >3 h; b) **2** and/or **3**, AcOH, DMSO; c) **18** and/or **19**, TFA, H_2O, DMSO; d) **24** or **25**, TFA, H_2O, DMSO, all at 40 ºC.

Interestingly, the absorption spectra of APIs stacked up on surfaces were different from that of monomers in solution: The lowest energy charge-transfer (CT) band became broader (full width at half maximum = 94 nm in DMSO, 123 nm in ***out*-1**) and bent to the higher energy side (Figure 4a). Similar features were previously observed for aligned APIs on TiO_2 surfaces with Li^+ additives, and rationalized with a Stark effect.[3c,3d,2b] Moreover, the excitonic coupling in H aggregates could contribute to the apparent blue shift of the absorption maxima, as observed in face-to-face stacked model API dimers.[3b] The absorption maximum of the *outward* dipolar photosystem ***out*-1** was at λ_{max} = 532 nm, almost as in DMSO, while that of the *inward* dipolar photosystem ***in*-1** was significantly blue shifted to λ_{max} = 520 nm. These results implied the presence of better π stacking interactions in ***in*-1** than in ***out*-1**. Preferential π stacking of inward dimers was also found with covalent perylenemonoimide dimers.[13c] The absorption maximum of ***mixed*-1** was with λ_{max} = 525 nm in-between dipolar ***out*-1** and ***in*-1**. This finding supported that the content of APIs **2** and **3** in ***mixed*-1** is roughly equal.

In ***mixed*-1**, hydrazones of **2** and **3** could form favorable antiparallel stacks by alternate self-sorting[7b,c,24] or form randomly mixed stacks containing also domains of parallel stacks. With TSE occurring under kinetic control, incomplete self-sorting into antiparallel stacks remains possible, and the indistinguishable spectroscopic signatures of parallel and antiparallel stacks did not provide insights on the extent of social self-sorting. However, equal incorporation of hydrazones of **2** and **3** assured that ***mixed*-1** does not contain global supramolecular dipolar fields.

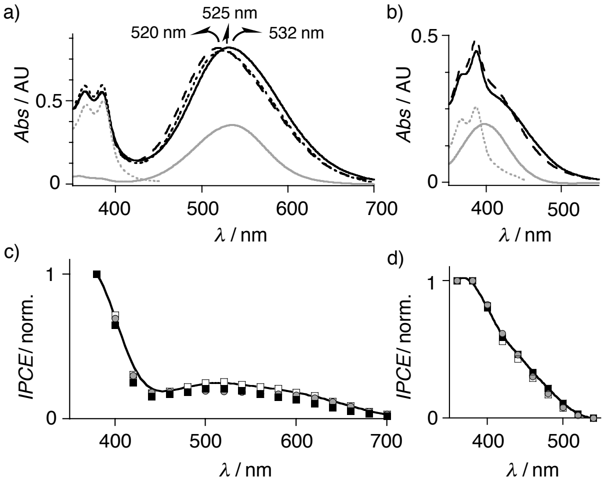


Figure 4. a) Absorption spectra before (gray dotted) and after addition of API **2** (solid, ***out*-1**), **3** (dashed, ***in*-1**) or **2** + **3** (dotted, ***mixed*-1**) to photosystem **22**, compared to **2** in DMSO (gray solid). b) Absorption spectra of photosystems before (gray dotted) and after TSE with a mixture of ANIs **18** and **19** (dashed), and after an equilibration in phosphate buffer (solid, ***mixed*-1N**) compared to **19** in DMSO (gray solid) as representative examples. c) Normalized action spectra of photosystems ***out*-1** (●), ***in*-1** (■) and ***mixed*-1** (□). d) Normalized action spectra of photosystems ***out*-1N** (●), ***in*-1N** (■) and ***mixed*-1N** (□).

The better soluble ANI aldehydes **18** and **19** were compatible with TSE conditions that operate under thermodynamic control, i.e., reversible hydrazone exchange in the presence of water and TFA to accelerate the rate determining hydrazone hydrolysis.[20] ANI aldehydes **18** and **19** gave photosystems with good TSE yields of ~70% for both ***in*-** and ***out*-1N** and 89% for ***mixed*-1N** (Scheme 2, Figure 4b). TSE yields under thermodynamic control with better soluble ANIs and kinetic control with less soluble APIs were in the same range, suggesting that the process reaches near completion under both conditions. TSE under thermodynamic control could favor alternate self-sorting in ***mixed*-1N**, thus maximizing the presence of antiparallel stacks and minimizing that of randomly mixed stacks. However, the spectral signature of ANIs was insensitive to antiparallel and parallel stacking. As with APIs in ***mixed*-1**, the extent of self-sorting into antiparallel stacks of ANIs in ***mixed*-1N** could not be quantified experimentally.

Due to the extensive overlap with NDI absorption, the CT band of ANIs appeared as a featureless, less informative broad shoulder in photosystems **1N** (Figure 4b, dashed spectrum). However, treatment of the photosystems with phosphate buffer to assure neutrality of hydrazone groups caused a clearly visible broadening or red shift of the CT band of the ANIs (Figure 4b, solid spectrum. The same buffer treatment of API photosystems resulted also in a red shift, although very small, i.e. ≤2 nm). The buffer treatment turned out to be important to obtain consistent and reproducible results in photocurrent measurements.

Photosystem Characterization. The dipolar photosystems were evaluated under routine conditions. Namely, the photosystems were used as working electrodes in the presence of triethanolamine (TEOA) as a mobile hole acceptor in solution, a Pt wire as a counter electrode, and Ag/AgCl as a reference electrode. Whereas the activities obtained with this assay are not comparable with data obtained from optoelectronic devices, they have been shown to reliably report correct trends under reproducible conditions.

Irradiated with a solar simulator, short-circuit photocurrents J_{SC} < 1 μA cm^{-2} were obtained with dipolar NDI-API photosystems (Figure 5a). These activities were overall clearly below the ones observed previously with macrodipole-free NDI-PDI photosystems under similar conditions.[9b,15] Low incident photon to current conversion efficiencies (IPCEs) found for APIs at ~500 nm compared to NDIs below 400 nm indicated that inefficient photoinduced electron transfer from API to NDI accounts for the weak activity (Figure 4c). This finding could be rationalized by the small LUMO energy difference between APIs and NDIs (Figure 3a).

With regard to photocurrent generation, the inward system ***in*-1** was more active than the outward system ***out*-1** (Figure 5a). Their normalized action spectra were nearly identical (Figure 4c). Bimolecular charge recombination efficiencies η_{BR} were determined from the dependence of photocurrents on irradiation power.[25] While the found η_{BR} were the same 42% for both systems upon excitation of APIs at ≥420 nm, full white light irradiation gave rise to slightly lower η_{BR} of 20% for ***in*-1** compared to 22% for ***out*-1** (Figure 5b). Activation energies E_a were determined from the temperature dependence of photocurrent generation.[15,26] Lower E_a was found with ***in*-1** than with ***out*-1** (Figure 5c).

Taken together, the slightly higher photocurrent generation of ***in*-1** coincided with slightly lower TSE yield, blue-shifted absorption maxima (Figure 4a), reduced charge recombination and shallower charge traps. These overall small changes in favor of ***in*-1** could indeed originate from the inward oriented dipolar fields but also from higher charge mobility in better π stacks, or from other effects. Most importantly, the found differences between double-channel photosystems with inward (***in*-1**) and outward (***out*-1**) oriented parallel API stacks were very small. Orientation independence has also been reported previously for APIs in DSSC.[3g]

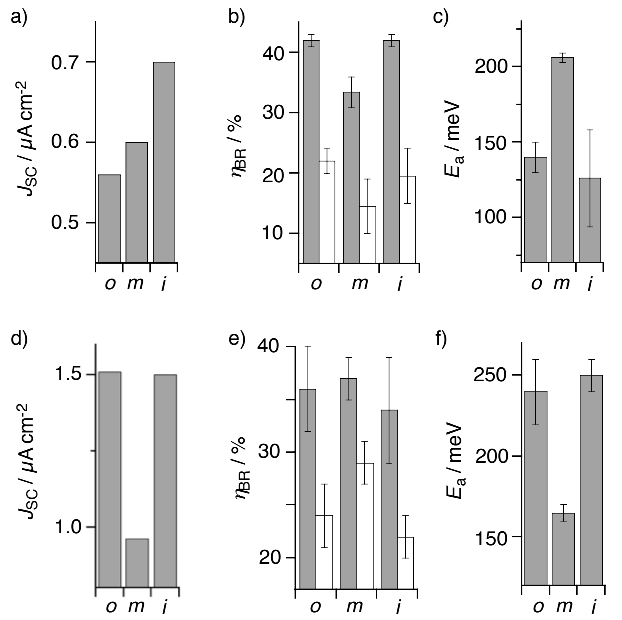


Figure 5. Characteristics of API (a-c) and ANI (d-f) photosystems ***out*-1(N)** (*o*), ***mixed*-1(N)** (*m*) and ***in*-1(N)** (*i*). a,d) Photocurrent generation upon irradiation with solar simulator. b,e) Bimolecular charge recombination efficiencies upon irradiation with white light (☐) or above 420 nm (■). c,f) Activation energies estimated from the temperature dependence of photocurrent generation. Results are of the SOSIP photosystems with similar absorbance (a,d) or the average ± error of data obtained with ≥2 independently prepared photosystems (b,c,e,f). Note that plots are scaled to highlight overall rather small differences.

Compared to API photosystems, ANI photosystems generated overall more photocurrent (Figures 5a, 5d). More efficient electron transfer from ANI to NDI was evident from comparable action and absorption spectra (Figures 4d, 4b). These results could be explained by a larger LUMO energy difference between ANI and NDI compared to API and NDI (ΔE_{LUMO} ≈ 0.77 *vs* 0.34 eV, Figure 3b). The difference in activity between ANI photosystems with *inward* (***in*-1N**) and *outward* (***out*-1N**) oriented parallel stacks was overall even smaller than with API photosystems (Figures 4d, 5d-f). These consistent trends with different push-pull components provided corroborative support that the orientation of parallel stacks in double-channel photosystems is irrelevant.

Compared to the dipolar photosystems ***in*-1** and ***out*-1**, ***mixed*-1** from the API series generated similar photocurrent with similar charge separation efficiency (IPCE, i.e., similar action spectrum, Figure 4c), clearly less charge recombination loss (η_{BR}, Figure 5b) and clearly higher activation energy (Figure 5c). In the ANI series, ***mixed*-1N** generated significantly less photocurrent than the dipolar systems ***in*-1N** and ***out*-1N** (Figure 5d). Moreover, ***mixed*-1N** generated photocurrent with more charge recombination loss (Figure 5e) but clearly lower activation energy (Figure 5f) than the dipolar ***in*-1N** and ***out*-1N**. These complementary trends are best understood considering that mixed ANI photosystems ***mixed*-1N** were prepared under thermodynamic control, whereas mixed API photosystems ***mixed*-1** had to be prepared under kinetic control. The compared to dipolar ***in*-1** and ***out*-1** only weakly reduced photocurrent generation of ***mixed*-1** with increased E_a and reduced η_{BR} was thus consistent with less organized architectures in more randomly mixed stacks of APIs. The more significantly reduced activity of ***mixed*-1N** with low E_a and high η_{BR} was consistent with tight stacking interactions between better self-sorted antiparallel stacks of ANIs.

Taken together, these findings suggested that the activity of mixed photosystems depends significantly on their method of preparation. Moreover, they support that the activity of double-channel photosystems with well-equilibrated and self-sorted antiparallel push-pull stacks is significantly lower than that with parallel stacks.

Dipolar Triple-Channel Photosystems. In double-channel photosystems, parallel stacks of push-pull components were identified as more powerful than antiparallel stacks, whereas the orientation of these parallel stacks turned out to be almost irrelevant. To elaborate on the orientation of dipolar stacks in triple-channel architectures, photosystems ***in*-23** and ***out*-23** were designed (Figure 6). Reminiscent of donor-bridge-acceptor type triads,[4d,13b,27] triple-channel photosystems could undergo photoinduced charge separation with electrons and holes in two differently substituted NDIs. The parallel push-pull stacks placed in between have their dipolar fields oriented toward the central n channel in ***in*-23** and toward the peripheral p channel in ***out*-23**.

Dipolar dyads **24** and **25** were prepared by amide bond formation between ANIs and *NN*-NDIs, i.e., NDIs with amine donors in the core. Interestingly, the absorption maxima of *NN*-NDIs in dyads were slightly (2 nm) shifted to blue (**25**) and red (**24**) compared to the parent *NN*-NDI (Figure S5). An appealing explanation of this finding is the stabilization and destabilization of LUMO of *NN*-NDIs by the nearby positive and negative end of the ANI dipoles, respectively. Similar Stark shifts have been observed in other dipolar systems.[5b]

These small shifts of the *NN*-NDI absorption maxima were conserved in triple-channel photosystems ***in*-23** and ***out*-23** (Figure 7a). They were obtained from SOSIP architecture **22** by hydrazone formation with aldehydes **24** and **25** (Scheme 2, Figure 6). Only moderate 40~50% of TSE yields could be achieved for these photosystems, probably due to the large size of the aldehydes (Figure 7a).

Upon solar irradiation, the outward triple-channel photosystem ***out*-23** generated significantly more photocurrent than the inward system ***in*-23** (Figure 7b). This finding was remarkable because ANIs in ***out*-23** are oriented in the opposite way from those found in the most donor-bridge-acceptor type triads.[4d,13b] Apparently, the distances between neither the donors (*NN*-NDI and HOMO of ANI) nor the acceptors (NDI and LUMO of ANI) influenced activity significantly (Figure 6). Moreover, dipole-induced acceleration or deceleration of charge separation could be excluded as a likely origin of the differences in activity because the nearly identical normalized action spectra demonstrated that relative contributions from each of chromophores to photocurrent generation are similar in the two systems (Figure 7c). However, charge recombination was significantly affected by the orientation of dipolar ANIs (Figure 7d). Whereas charge recombination efficiencies η_{BR} were almost the same for both systems upon excitation of only *NN*-NDIs at ≥520 nm, they were clearly higher for ***in*-23** when ANIs were also irradiated. This quite remarkable "optical gating" suggested that

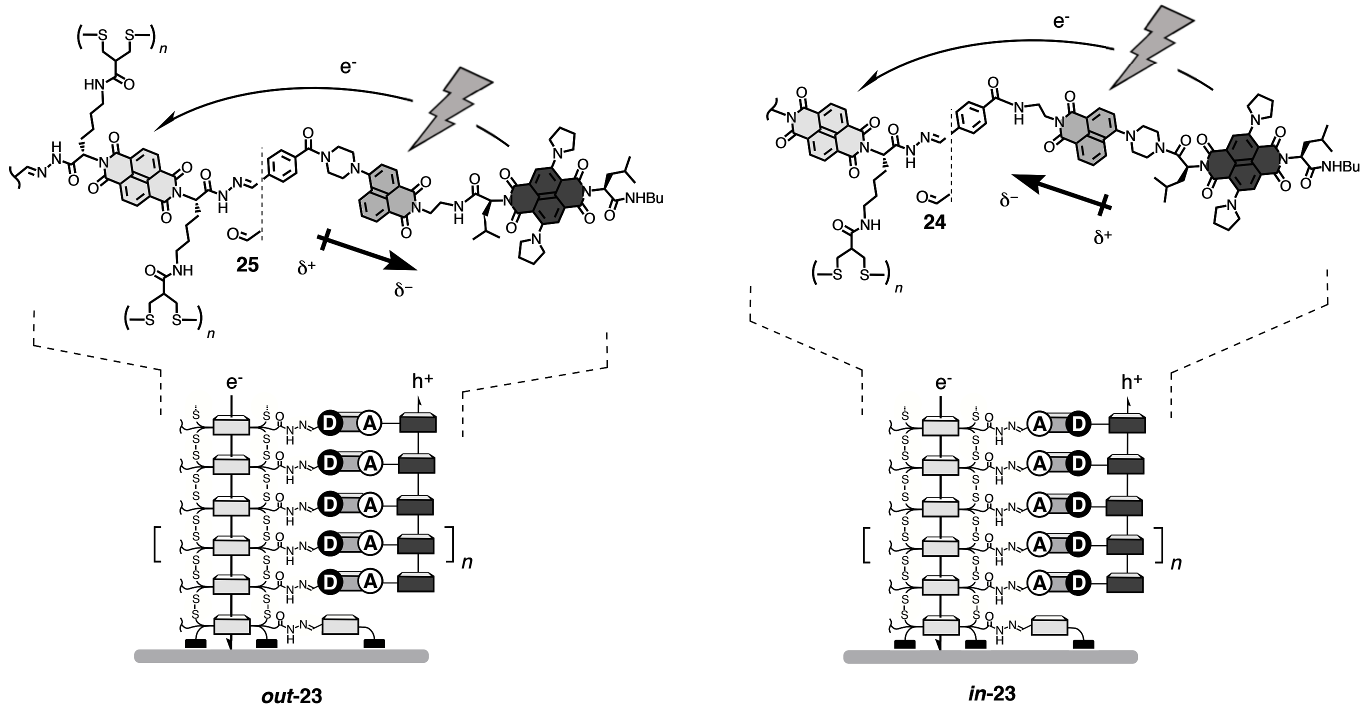


Figure 6. Schematic, idealized structure of dipolar triple-channel architectures with macrodipoles in the ANI stack pointing away from and toward the central NDI stack in photosystems ***out*-23** and ***in*-23**, respectively.

the charge-separated state of ***in*-23** is destabilized by wrongly oriented strong excited-state dipoles of ANIs, while ground-state dipoles are too weak to result in a detectable effect. The complementary stabilization of the charge-separated state by strong supramolecular dipolar fields with excited-state push-pull dipoles (Figures 7d, 6) should then account for the high activity of the matched triple-channel photosystem ***out*-23** (Figure 7b).

Conclusions

In summary, SOSIP-TSE strategy allowed us to dissect the inherent and supramolecular properties of dipolar compounds in photocurrent generation. Oriented in parallel manner in double-channel photosystems, inward or outward direction of push-pull dyes did not matter much for photocurrent generation. In mixed systems, dipolar dyes in random or antiparallel orientations gave reduced activities. Thus, in double-channel systems, the effect of dipoles is primarily on the supramolecular organization, which in turn determines photocurrent generation, while their direct influence on charge separation or recombination is minimal.

In triple-channel photosystems, however, charge recombination was greatly affected by the orientation of the supramolecular dipolar field of parallel push-pull stacks in between stacks of acceptors and donors, particularly when directly irradiated. Such "optical gating" of photosystems significantly influences photocurrent generation and is thus particularly interesting for future developments. With molecular triads in solution, Wasielewski and coworkers reported similar "optical switches".[27] Namely, the excitation of a dipolar bridge in the triad was shown to reduce the lifetime of a charge separated state.[27a] With dipolar triple-channel architectures on solid surfaces, "optical gating" could so far not be explored because the synthetic methods to build the required complex systems have not been available before the introduction SOSIP-TSE. However, higher TSE yields will be desirable to facilitate data

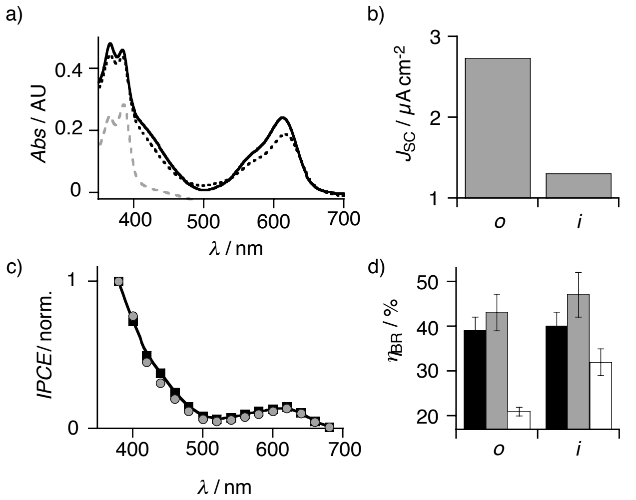


Figure 7. a) Absorption spectra before (gray dotted, **22**) and after reaction of ANI-*NN*-NDI **24** (dashed, ***in*-23**) and **25** (solid, ***out*-23**) with photosystem **22**. b) Photocurrent generation by ***out*-23** (*o*) and ***in*-23** (*i*) upon irradiation with solar simulator. c) Normalized action spectra of photosystems ***out*-23** (●) and ***in*-23** (■). d) Bimolecular charge recombination upon irradiation of ***out*-23** (*o*) and ***in*-23** (*i*) with white light (open), ≥ 420 nm (gray) or ≥ 520 nm (black filled). Results are of photosystems with similar absorbance, error bars refer to curve fit.

interpretation. Studies toward controlling interstack distances are ongoing to solve this general problem with larger stack exchangers.

Otherwise routine characterization of the push-pull monomers prepared for the construction of dipolar photosystems by SOSIP-TSE indicated that their unusual spectroscopic properties in ionic liquids might originate from ion pair-π interactions.

Acknowledgements

We thank K.-D. Zhang, M. Macchione and D.-H. Tran for contributions to synthesis, D. Jeannerat, M. Pupier and S. Grass for NMR measurements, the Science Mass Spectroscopy (SMS) platform for mass spectrometry service, and the University of Geneva, the European Research Council (ERC Advanced Investigator), the National Centre of Competence in Research (NCCR) in Chemical Biology, the NCCR Molecular Systems Engineering, and the Swiss NSF for financial support.

Keywords: Dipolar photosystems • orthogonal dynamic covalent bonds • disulfide exchange • hydrazone exchange • surface-initiated polymerization • push-pull chromophores • ionpair-π interactions

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Received: ((will be filled in by the editorial staff))
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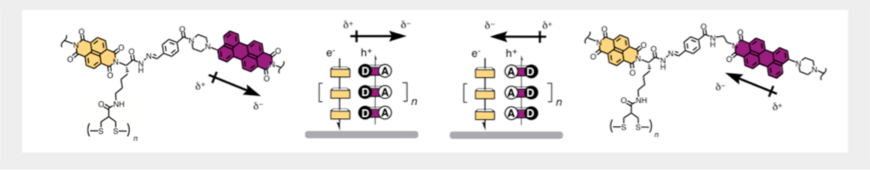

Oriented Macrodipoles: Synthetic access to ordered multicomponent architectures is applied to explore dipolar photosystems. Whereas mixed stacking is confirmed to be unfavorable, the direction of parallel dipoles had surprisingly little effect on the photocurrent generation by double-channel photosystems. In triple-channel architectures, more significant optical gating was found upon direct irradiation of the oriented dipolar stacks between the stacks of donors and acceptors.

Supramolecular Chemistry

*Altan Bolag, Naomi Sakai and Stefan Matile**

■■ – ■■

Dipolar Photosystems: Engineering Oriented Push-Pull Components into Double- and Triple-Channel Surface Architectures