Rigid-rod push–pull naphthalenediimide photosystems†

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Design, synthesis and evaluation of advanced rigid-rod π-stack photosystems with asymmetric scaffolds are reported. The influence of push–pull rods on self-organization, photoinduced charge separation and photosynthetic activity is investigated and turns out to be surprisingly small overall.

The design and synthesis of advanced optoelectric nanomaterials is a topic of current scientific interest.1–18 In this report, we describe the synthesis and characteristics of push–pull p-octophenyl 1, a rigid-rod molecule that carries blue naphthalenediimides (N,N-NDIs) along the rigid-rod scaffold, a π-donating methoxy at one rod terminus and a π-accepting amide plus a negative charge at the other (Fig. 1). Compared to the previous photosystems 2 and 3,16–18 the new push–pull rod 1 contains a macrodipole along the rigid-rod scaffold. This axial macrodipole was of interest to explore the possibility of controlling photosynthetic and photophysical characteristics of 2 and 3 such as stabilization of the symmetry-breaking2–16 photoinduced charge separation. These effects would be amplified with the parallel self-assembly of rod 1 into π-M-helix 4. This supramolecule might form in lipid bilayers because of hindered translocation of the anionic carboxylate anchors across the membrane. In solution, dipole–dipole attraction should cause antiparallel self-assembly into quadruple π-M-helix 5 with reduced effects. These high expectations appeared meaningful considering the extensive evidence for remote control of optoelectric properties by α-helical macrodipoles. Highlights include fluorescence quenching in donor–acceptor dyads by α-helical dipoles,19 amplified dark current along single α-helical dipoles,20 and amplified photocurrents across monolayers of parallel α-helices on gold.1 Moreover, rigid push–pull rods have been of use previously to create several variations of voltage-gated ion channels.21–22

The synthesis of rod 1 is summarized in Scheme 1. The p-sexiphenyl 6 was envisioned as an ideal building block to attach the π-attracting and π-donating rod termini 7 and 8, respectively, and the blue N,N-NDIs 9 along the rigid-rod scaffold. Rapid access to p-sexiphenyl 6 from the commercially available biphenyl 10 and tert-butyl bromoacetae 11 has been reported previously.23 Last year, we also synthesized N,N-NDI 9 starting with oxidation of pyrene 12, reaction of the resulting dichlororhodanidine first with amines 13, 14 and then with 15 to give 16, followed by chemoselective removal of Alloc.16 Rod terminus 7 was synthesized from benzaldehyde 17, which was converted into iodinated compound 18 in four steps.24 After acidic deprotection, benzaldehyde 19 was reacted first with tert-butyl bromoacetae 11, followed by oxidation. Coupling of the resulting acid 20 with C-protected glycine 21 gave the desired π-accepting amide 22 with a protected carboxylate anchor. Pina-colboronate 23 was obtained by Pd-catalyzed conversion of aroyl iodide 22.25 It was directly converted to the pull-fragment 7 with KH5F to benefit from increased stability, easier purification and higher reactivity of potassium trifluoroborates.26–27

The push-fragment 8 was synthesized from phenol 24. The previously reported ortho-iodination gave pure regioisomer 25,27 which was subjected to Williamson ether synthesis with tert-butyl bromoacetae 11. The obtained aroyl iodoide 26 was transformed via boronate 27 into the desired, air-stable and solid potassium trifluoroborolate 8.

Pull-fragment 7, push-fragment 8 and chromophores 9 were coupled sequentially to p-sexiphenyl 6. Suzuki coupling of p-sexiphenyl 6 first with push-fragment 8 gave p-septiphenyl 28 in 42% conversion yield, subsequent attachment of the pull-fragment 7 at the other terminus gave the final push–pull rod 29. The lateral tert-butyl esters in 29 were cleaved with TFA without damage to the terminal benzyl esters. The liberated carboxylic acids along the rigid-rod scaffold of 30 were reacted with eight N,N-NDI amines.
Scheme 1  
(a) Four steps, see ref. 23. (b) HCl (aq), THF, 88%. (c) 1. Cs2CO3, DMF, 91%; 2. NaClO2, NaH2PO4, H2O2, 91%. (d) HATU, iPr2NEt, quant. (e) Pinacolborane, PdCl2(dppf), Et3N, CH3CN, 1 h, reflux. (f) KHF2, MeOH–H2O, 2 h, rt, 47% from 22. (g) AgOTf, I2, CHCl3. (h) Cs2CO3, DMF, 92%. (i) Pinacolborane, PdCl2(dppf), Et3N, CH3CN, 1 h, reflux, 88%. (j) KHF2, MeOH–H2O, 2 h, rt, quant. (k) PdCl2(dppf), Et3N, MeOH–THF 1 : 1, 30 min, reflux, 25%, conversion yield 42%. (l) PdCl2(dppf), Et3N, MeOH–THF 5 : 1, 30 min, reflux, 49%, conversion yield 66%. (m) TFA, CH2Cl2, 30 min, rt. (n) HATU, Et3N, 2,6-di-tBu-pyridine, DMF, rt, 24 h, 75% from 29. (o) HBr, AcOH, TFA, thioanisole, pentamethylbenzene, 90 min, rt, quant. (p) Five steps, see ref. 22. (q) Four steps, see ref. 16. (r) Bu3SnH, Pd(PPh3)2Cl2, CH2Cl2, rt, 30 min, 86%, see ref. 16.

9, and the obtained conjugate 31 was fully deprotected with HBr–AcOH to give target molecule 1.

The hypsochromic shoulder of the band around 600 nm in the absorption spectrum of the push–pull system 1 ↔ 5 was indicative of face-to-face π-stacking of the N,N-NDI chromophores.2,16 The bisignate CD Cotton effect of this transition supported self-organization with M-helicity (Fig. 2C).16,17 Strong in iso-propanol, intermediate in methanol (MeOH) and weak in 2,2,2-trifluoroethanol (TFE), both effects exhibited identical solvent dependence (Fig. 2B). Unrelated to solvent polarity (Fig. 2A), this trend could reflect self-assembly of rod 1 into antiparallel π-helix 5 in isopropanol and MeOH but not as much in TFE.

In MeOH, push–pull system 1 (Φf = 4 × 10−4) was 20-times less fluorescent than the symmetric control 2 (Φf = 9 × 10−3). The same weak emission was found for 1 in vesicles. This effect could imply more efficient photoinduced charge separation along the macrodipole in monomeric 1. Alternatively, dipole–dipole attraction might promote antiparallel self-assembly, and increased charge separation might be the result of an increased concentration of π-stacked N,N-NDI chromophores in π-helix 5. Moving from MeOH to TFE, the quantum yield of push–pull system 1 (Φf = 3 × 10−4) did not change significantly. This independence on partial disassembly of π-helix 5 into 1 suggested that indeed the macrodipole contributes to photoinduced charge separation in monomer 1.

The early fluorescence dynamics were monitored using the fluorescence up-conversion technique (400 nm excitation, 100 fs pulses). In all cases, fluorescence decay was highly non-exponential, and at least 5 exponential functions were needed to reproduce the fluorescence decay. The average lifetime of push–pull system 1 (τav = 20–50 ps) was 4- (in MeOH) to 15-times (in TFE) shorter than that of the symmetric control 2 (τav = 200–310 ps). Particularly, the extent of ultrafast decay within the first 15 ps for push–pull system 1 (89% in MeOH, 76% in TFE) compared to 2 (66% in MeOH, 56% in TFE) could be interpreted as accelerated charge separation in push–pull photosystem 1 (Fig. 3A).

Fig. 2  Relative absorption of hypsochromic shoulder/absorption maximum in the absorption spectra (A, B) and amplitude Δν in the CD spectra of 1 (A, C) in, with decreasing dielectric constant, MeCN, MeOH (red), TFE (blue), isopropanol (purple) and THF. (C) Original CD spectra in isopropanol (purple), MeOH (red) and TFE (blue).

Fig. 3  Intensity-normalized time profiles of (A) fluorescence decay and (B) decay of the transient N,N-NDI− absorption of 1 (△) and 2 (○) in TFE. For full data sets, see ESI.
The existence of photoinduced charge separation was confirmed by the transient absorption of the \(N,N\text{-NDI}^+\) radical anion at 510 and above 670 nm following excitation with a 50 fs laser pulse at 610 nm.\(^{16}\) According to the decay kinetics of the \(N,N\text{-NDI}^+\) radical anion, the lifetime of the photoinduced charge-separated species of push–pull system 1 (MeOH: \(\tau = 50\) ps, TFE: \(\tau = 40\) ps, Fig. 3B) was quite similar to that of the blue control 2 (MeOH: \(\tau = 65\) ps,\(^{16}\) TFE: \(\tau = 50\) ps) but clearly, about 10-times shorter than that of the red control 3 (MeOH: \(\tau \approx 500\) ps\(^{16}\)). This suggested that, in contrast to accelerated charge separation, scaffold asymmetry in push–pull photosystem 1 did not affect charge recombination much.

The delivery of functional nanoarchitecture to bilayer membranes is an underrecognized and underexplored process that often determines the finally observed apparent activities.\(^{29,30}\) For membrane delivery, concentrated solutions in various solvents (and eventual additives) are simply added to the vesicle suspension, and for the functional compounds are hoped to reach the membrane before precipitation. To determine the solvent that best delivers photosystem 1, large egg yolk phosphatidylcholine vesicles (EYPC LUVs) were labeled with lipid-bound NBD by FRET to \(N\)-membrane NBD (\(t = 463\) nm, \(\tau = 535\) nm). Quenching of lipid-bound NBD by FRET to \(N\)-NDIs indicates the relative quantity of delivered photosystem 1. With the disassembling TFE as best (●) and the assembling MeOH as worst transporter (○), significant differences were found in the ability of solvent additives to deliver photosystem 1 to EYPC LUVs. Controls with monomeric \(N\)-NDIs 9a (○)\(^{16,18}\) confirmed that poor delivery by MeOH is compound-specific and not intrinsic (Fig. 4A).

4 ↔ 5 exhibited no cooperativity under the present conditions.\(^{17}\) Different to both symmetric controls, this finding suggested that the introduced asymmetry has a negative effect on the formation of active self-assembly. Facilitated antiparallel self-assembly into the hydrophobic \(\pi\)-helix 5 by dipole–dipole attraction before reaching the membrane could explain both poor activity and lack of cooperativity. Alternatively, these results could also be explained by hindrance of parallel self-assembly into 4 by dipole–dipole repulsion in the membrane. Moreover, vectorial control of partitioning by the terminal carboxylate might be lacking or opposite to expectations. Overall, we caution that a number of pathways to the functional system are conceivable to account for the reduced activity and cooperativity found with push–pull photosystems.

In summary, the introduction of asymmetry in photoactive rigid-rod \(\pi\)-stack nanoarchitecture is found to reduce fluorescence, to accelerate photoinduced charge separation, but to have little effect on charge recombination. These overall favorable properties, however, were not reflected in higher photosynthetic activity in lipid bilayer membranes. Hindered formation of the active suprastructure might account at least in part for these overall complex and surprisingly small effects. We conclude that vectorial self-assembly of asymmetric photosystems in lipid bilayers will be very challenging.

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Notes and references