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Molecular electrets – Why do dipoles matter for charge transfer and excited-state dynamics?

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ABSTRACT

For decades, the natural systems, and in particular photosynthesis, have provided the principal paradigms for solar-energy science and engineering. Charge transfer (CT) is at the core of life-sustaining biological processes, including the natural energy conversion and storage. Concurrently, nanoscale CT govern the performance of electronic and energy-conversion devices. Electric fields are invaluable for guiding charge movement. Therefore, as electrostatic analogues of magnets, electrets have unexplored potential for generating local electric fields for accelerating desired CT processes while suppressing undesired ones. This publication presents the design principles and the development of CT bioinspired molecular electrets, along with some of the synthetic challenges for obtaining the optimal motifs. We discuss these advances in the contexts of how dipoles affect CT and excited-state dynamics. The underlying complexity of dipole-induced effects reveals unexplored paradigms for CT science, as well as for electronic and optical engineering. The ubiquity of electric dipoles underlines the immense potentials that electrets have for electronics, photonics and energy-conversion.

1. Introduction

The anthropologic activities have brought our planet to the verge of an ecological catastrophe [1]. Constantly-growing global energy consumption, essential for sustaining our modern ways of living, presents a principal threat for the world as we know it. Therefore, energy challenges are still a priority that requires a global approach [2,3].

With an average flux of about 200 W m^{-2} at the surface of the planet, sunlight is an abundant energy source [4]. Harvesting just a small fraction of it and converting it into a useful form, such as electricity or fuels, provides an incomparable means for meeting the global energy demands in an environmentally benign manner [5]. A range of challenges, such as the orthogonality between cost and power-conversion efficiency, prevents solar from becoming a vital energy technology [6]. New paradigms from research are essential for driving the development of energy sustainability.

Over the millennia of evolution, photosynthesis evolved to harvest solar energy and utilize it for the anabolism of caloric substances, thus, storing it in a form of biological fuels essential for sustaining life on Earth [7–9]. The photosynthetic systems, therefore, offer excellent paradigms for solar-energy science and engineering. Mimicking photosynthesis provides a means not only to further the solar-energy science, but also to test and elucidate key aspects of the biological light harvesting [10]. Taking the ideas for light harvesting, energy storage and energy conversion outside of their biological context, illustrate the bioinspired approaches that can bring the field beyond what nature can offer [11,12].

Charge transfer **(CT)** is the most important process for every step of energy conversion from light harvesting to energy storage, and to utilization. Therefore, energy research, in the pursuit of artificial photosynthesis and solar fuels, has been a principal driving force for the development of CT science [11–15]. The ability to enhance forward CT while suppressing undesired processes, such as charge recombination **(CR)**, is a "holy grail" for energy conversion.

Electric dipoles are ubiquitous and the localized fields they generate affect the transfer of charges. Understanding the dipole effects on CT, therefore, opens doors to important new paradigms for energy science and engineering. As the electrostatic analogues of magnets, electrets offer the best means for such a line of research and development.

Electrets are systems with ordered electric dipoles. Therefore, electret materials inherently are electrical insulators. Free charge carriers readily redistribute and screen the dipole-generated fields. At the same time, electrets should mediate efficient CT in order to utilize their dipole effects on charge transduction. This conundrum has impeded

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the growth of the field, even though the first reports about dipole effects on CT appeared in the 1960s [16,17].

Biology offers the best examples of molecular electrets in the form of protein helices [18–20]. Concurrently, life depends on processes involving long-range CT mediated via hopping by insulating biomacromolecular and supramolecular structures [21]. Bringing together these two natural paradigms allowed us to develop bioinspired CT molecular electrets, based on anthranilamide **(Aa)** oligomers (Fig. 1), the exploration of the potentials of which is still in its infancy.

This publication discusses the design principles and the development of CT molecular electrets, along with some of the synthetic challenges for obtaining the optimal motifs. We present these advances in the contexts of how dipoles affect CT. Solar-energy research has been, indeed, a key driving force for the evolution of CT science and the research on dipole-modulated CT. Nevertheless, the impacts of dipoles on charge transduction, excited-state dynamics and other phenomena expand considerably beyond energy science and are as broad as they are important.

1.1. Charge transfer, charge separation and charge transport: what's the difference?

Before immersing into the subject matter of this feature article, it is a good idea to briefly review the fundamental concepts and terminology of CT science.

Charge transfer, CT, involves movement of charges from one moiety to another. These moieties can be parts of the same molecule or different spatially separated species. Such movement of electrons or protons represents, respectively, electron transfer **(ET)** or proton transfer **(PT)**. When ET involves a transfer of an electron from an occupied orbital of a donor to a singly-occupied orbital of an acceptor, it can represent hole transfer **(HT)** from the acceptor to the donor. The distinction between ET and HT becomes important for long-range CT. Involvement of unoccupied orbitals of the moieties between the donor and the acceptor define ET; and involvement of occupied orbitals – HT [21].

ET from a non-charged electron donor to a non-charged electron acceptor results in charge separation **(CS)**. That is, the positive and the negative charges maintaining the electroneutrality got separated. ET between a donor that is positively charged and an acceptor that is negatively charged also leads to CS. CS results in an increase of the total positive charge of the donor and the total negative charge of the acceptor [21].

ET involving a non-charged donor and a positively-charged acceptor results in a charge shift **(CSh)** [22,23]. Movement of an electron from the donor to singly-charged acceptor effectively results in shifting the positive charge of the acceptor to the donor. Similarly, ET from a negatively charged donor and a non-charged acceptor also leads to CSh, i.e., of the negative charge of the donor to the acceptor. When the donor is negatively charged and the acceptor is positively charged, ET results in a decrease, or complete elimination, of the charges on these species, leading to charge annihilation **(CA)** [21]. While CA resembles charge recombination, CR, they represent different processes. CR depicts the deactivation of a CT state leading to the ground, initial, states of the donor and the acceptor. CA, on the other hand, leads to CT states,

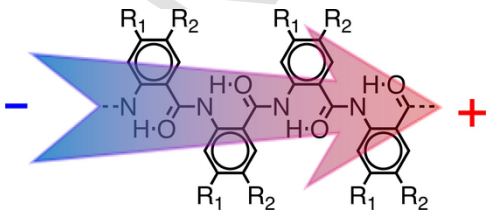


Fig. 1. Bioinspired molecular electret with its macrodipole pointing from its N-terminus to its C-terminus.

in which the donors and the acceptors may be non-charged, but they are still energetically rich. For example, starting with a charged singlet donor and an acceptor, CA leads to radial formation: $[^1D– + {}^1A^+]^* \rightarrow D^\bullet + A^\bullet$.

While CT, ET, HT, PT, CS, CSh and CA are processes describing movement of charges, they also designate states. A CT process leads to the formation of a CT state, or a state with a CT character. Is it customary to think that an increase in the medium polarity stabilizes states with a CT character and favors their formation? This notion is valid when CT involves CS, and leads to states with a CS character. CS causes an increase in the electric dipole moment in a donor-acceptor system, and even in generating a dipole. Proportional to the reaction field in a solvated cavity, the Onsager solvation energy, $\Delta G_O \propto -((\varepsilon - 1) / (2\varepsilon + 1))\ (\boldsymbol{\mu}^2 / r^3)$, show how an increase in the solvent polarity, represented with the dielectric constant ε, stabilizes species with a dipole moment $\boldsymbol{\mu}$ and a radius r [21,24–26]. Conversely, when the donor and the acceptor are spatially well separated, the Born solvation energy, $\Delta G_B \propto -((\varepsilon - 1) / \varepsilon))\ (q^2 / r)$, illustrates how solvent polarity stabilizes separately the donor and the acceptor with charges q [24–26]. Regardless the spatial distance between the donor and the acceptor, polar medial lowers the energy levels of CS states.

This medium-polarity trend is completely opposite for CA. Because CA leads to a decrease in the magnitudes of the charges on the donor and the acceptor, lowering the solvent polarity lifts the energy levels of CT states that originate from CA.

For CSh, the polarity effects can go either way. While the reorganization energy, needed for accommodating the movement of the charges, affects the CT kinetics, CSh does not change the charge and does not really lead to formation or depletion of dipole moments. Nevertheless, the Born solvation energy is inversely proportional to the radius of the charged species, $\Delta G_B \propto -r^{-1}$ [24], which induces polarity dependence for the thermodynamics of CSh between a donor and an acceptor with different sizes.

For CSh from a small to a large moiety, an increase in solvent polarity decreases $-\Delta G_B$ and destabilizes the CT state. It is evident, for example, from polarity-induced hypsochromic shifts in direct $S_0 \rightarrow$CT optical transitions to SCh states with wider charge delocalization than the S_0 states [22]. Conversely, when CSh involves a transfer of a charge from large to small species, medium polarity stabilizes the formed CT state. An important consideration when thinking of CSh, and in general of CT, is the treatment of the counterions. Electrostatically tightly bound counterions can change the CSh regime to a CS one [21].

Another important consideration that tends to complicate the analysis of CT thermodynamics involves the definition of the radii, r, of the donor and the acceptor. The Born, Kirkwood and Onsager solvation models describe dipolar and charged species with spherical symmetry, or at least placed in spherical solvation cavities. Spheres are a good approximation for the shapes of fullerenes and many metal chelates. Most molecules, however, are not spherical, and especially when charges of ionic species are not equally distributed, the donor and the acceptor radii, r, can be ill-define. Generalized Born radii, on the other hand, account for the shapes of the donor and the acceptor and for the atomic-level charge distribution before and after the CT steps [26].

In all these cases of various types of CT, the transitions involve donor and acceptor states with well defined orbitals. This notion is readily extendable to interfacial CT, where ET and HT occurs between orbital of redox species and the bands of electrode substrates. Taking this way of thinking a step further and replacing both, the donor and the acceptor, with electrodes, results in systems that mediate transport of electrons and holes between the bands (or multiple states) of the substrates. Charge transport **(CTr)** describes such transduction of electrons and holes through and between conductors and semiconductors. When molecules span between conductive substrates, to form electric junctions, the currents through these molecules, under applied volt-

age bias, characterize their CTr properties. In contrast, rate constants describe CT.

Quantum confinement, leading to emergence of defined states, can blurs the distinctions between CT and CTr. For example, moving hot electrons or holes through Schottky junctions between metal plasmonic nanoparticles and a semiconductor nanocrystals is referred to as CT and characterized with rate constants [27].

CT and CTr are related. The electrical currents and the molecular conductivity relate to the rate constants of the CT processes that these molecules mediate. Band conductance, involving movement of electrons and holes through Fermi gas, governs CTr through metallic substrates. Similar to CT, however, charge hopping (or polaron hopping) is a form of the long-range CTr through a wide range of semiconductors, including metal oxides and perovskites [28–30].

Beyond electrons and holes, CTr encompasses transduction of a wide variety of charged entities. For solutions, CTr, or ion transport, defines electrolyte conductivity. Ion transport is of outmost importance for physiology and vital for the survival of living cells and organisms.

ET, HT, PT, CS, CSh, CA and CR describe different types of CT. As similar as CT and CTr may appear, they are different processes and interchangeable use would prove misleading.

1.2. Bioinspired molecular electrets

Following the first reports of dipole effects on CT [16,17,31,32], every few years new sets of publications testify for waves of growing interest in thins subject [33–53]. While much work focuses on small polar molecules at interfaces [33–44], reports on **long-range CT** utilize polypeptide helices as sources for macrodipoles [34,45,35–53], Polypeptide helices have enormous dipoles and they are easy to prepare by using automated solid-phase synthesis. Furthermore, polypeptide α-helices can readily form ordered self-assembled monolayers **(SAMs)** on solid substrates [45]. It has allowed the demonstration of dipole effects on interfacial CT and charge transport **(CTr)** [54,55].

The use of polypeptide conformers for CT scaffolds, however, poses some challenging limitations: (1) the conformational integrity of polypeptide α-helices is often compromised when taken out of their natural environment, thus limiting the scopes of their applications, and (2) injection of electrons or holes in polypeptides composed of natural α-amino acids leads to their reductive or oxidative degradation, respectively, preventing them from mediating CT via hopping. Along their backbones, therefore, polypeptides can mediate CT only via quantum mechanical tunneling, or superexchange mechanism, the rates of which exponentially decrease with distance [56–58]. As a result, the polypeptides cannot mediate efficient CT (initiated by excited states with nanosecond lifetimes) at distances exceeding much more than about 2 nm [55,58]. Conversely, incoherent charge hopping along (1) protein cofactors [59], (2) redox active amino acid side chains [60], and (3) π-stacked base pairs in polynucleotides [61], allows biomolecules and their assemblies to efficiently mediate CT at impressively long distances [59–62].

Combining the structural motifs of protein helices, responsible for the intrinsic macrodipoles, with the concepts of biological arrays that mediate long-range CT, we developed bioinspired molecular electrets based on Aa structures (Fig. 1). Similar to protein helices, ordered amide and hydrogen bonds generate macrodipoles along the backbones of the Aa oligomers (Fig. 1) amounting to about 3 debyes per residue [63,64]. Unlike proteins and synthetic polypeptide helices, however, aromatic moieties, directly linked with amide bonds, provide sites for electron or hole hopping that are essential for attaining long-range CT. The electric fields resultant from such ordered dipoles can visibly affect the CT processes they mediate. That is, the dipole-generated local electric fields can serve as important tools for accelerating desired CT processes, while suppressing undesired ones, which is paramount for conversion and storage of harvested solar energy.

While two decades ago our focus was on biomimetic CT systems based on polypeptides of native amino acids [57,58,65–68], for the last 10 years, we have undertaken a bioinspired approach in designing molecular electrets that have important structural and functional advantages over their biological counterparts. At the beginning of this adventure, the anthranilamide motif attracted our attention. These synthetic Aa macromolecules, which are aromatic oligo-*ortho*-amides with their extended structures supported by a hydrogen-bond network (Fig. 1), are perfectly suited for molecular engineering of bioinspired molecular electret. While the structural features of Aa oligomers have been the focus of previous investigations showing the extended conformation from X-ray crystallography analysis [61], their electronic properties were unknown prior our work in this field. Theoretical studies allowed us to gain insights into the electronic properties of these compounds [64]. These studies show intrinsic dipole moments oriented along the polymer axes, which increase with the increase in the length of the Aa oligomers. Each amide bond contributes about 2 D to the macromolecular dipole. While amides are some of the most polar small groups in biomolecules with permanent dipoles ranging between 3.5–5 D [70], their angular orientation in the Aa structures decreases their contribution to the axial macrodipoles (Fig. 1). In addition, the polarization during hydrogen bonding, involving shift of electron density from the carbonyl oxygens to the hydrogens of the adjacent amides, enhances the macrodipoles by extra 1 D per residue (Fig. 1) [70].

When we add electron donating and electron withdrawing groups we observe that: (1) these side chains further polarize the aromatic residues, change the magnitude and sometime the orientation of the macrodipoles; and (2) extension of the π-conjugation over some of these side chains narrows the HOMO-LUMO gaps, i.e., the gaps between the highest occupied molecular orbitals and the lowest unoccupied molecular orbitals. Unlike in protein α-helices, the internal dipoles of the Aa oligomers point from their N- to their C-termini.

Having theoretical results in hands, we verify these findings experimentally focusing on the fundamental Aa structures, i.e., $R_1 = R_2 =$ H [63]. Indeed, impedance spectroscopy reveals that anthranilamides are molecular electrets, possessing intrinsic dipole moments, oriented from their N- to their C-termini as confirmed by NMR analysis, which agrees with the theoretical findings [63]. Furthermore, these Aa structures manifest a large propensity for self-assembly [63].

To determine whether Aa dipoles can affect CT, we compare the rates of ET towards the C-termini versus the N-termini of an electron-rich Aa residue [71]. Specifically, we construct dyads comprising Aa as an electron donor and 1-alkylpyrene (Py) as an electron acceptor (Fig. 2).

These donor-acceptor dyads distinctly rectify not only the forward photoinduced ET, but also the subsequent CR, which was a key step forward in the field of dipole-modulated CT (Fig. 3) [71]. Our findings show that charge separation **(CS)** is faster when the electron moves along the dipole than when it moves against it, which perfectly agrees with the accepted notion for the dipole effects on the CT driving forces, $-\Delta G^{(0)}$. The CR rates were also larger when the electron moved along the dipole than against it.

The observed rectification of CS decreases with an increase in medium polarity, which is consistent with screening of the dipole-generated localized electric field [63]. It is consistent with the origin of the CS rectification from the Aa permanent electric dipole. The rectification of CS, however, originates from an interplay between the dipole effect on $\Delta G_{CR}^{(0)}$ and the donor-acceptor electronic coupling [71].

These immensely encouraging results set the foundation for developing a broad variety of Aa residues with diverse electronic and optical features (Fig. 4) [72–76]. Variations in the single side chain of native α-amino acids defines the countless structural and functional character-

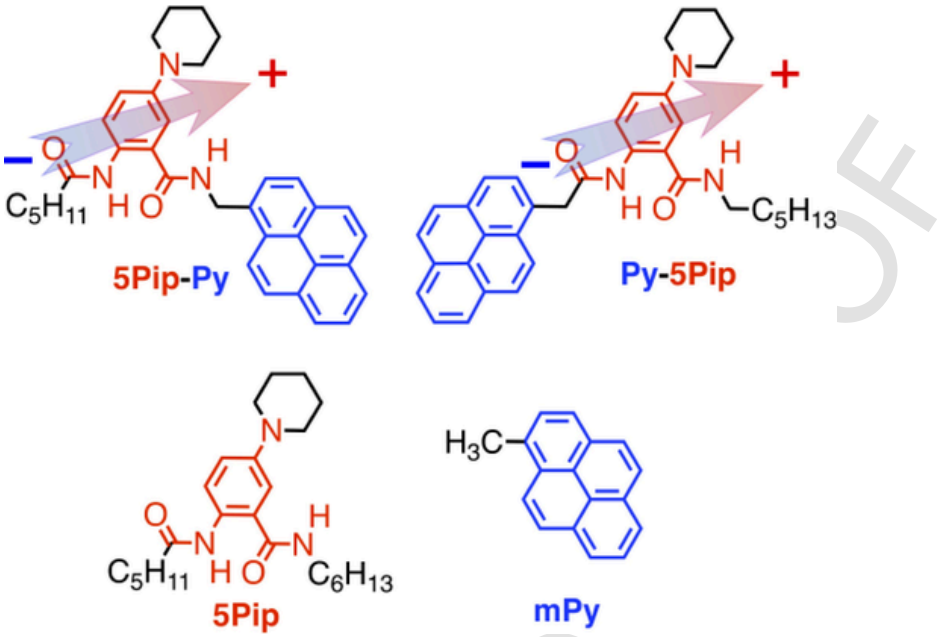


Fig. 2. Donor–acceptor dyads with the acceptor, pyrene (Py), linked to the C-terminus (Py-5Pip) and the N-terminus (Py-5Pip) of an electron-rich anthranilamide residue, 5Pip, which is also the electron donor [71]. The arrows on the structures of the dyads represent the orientation of the permanent dipoles of the anthranilamide residue.

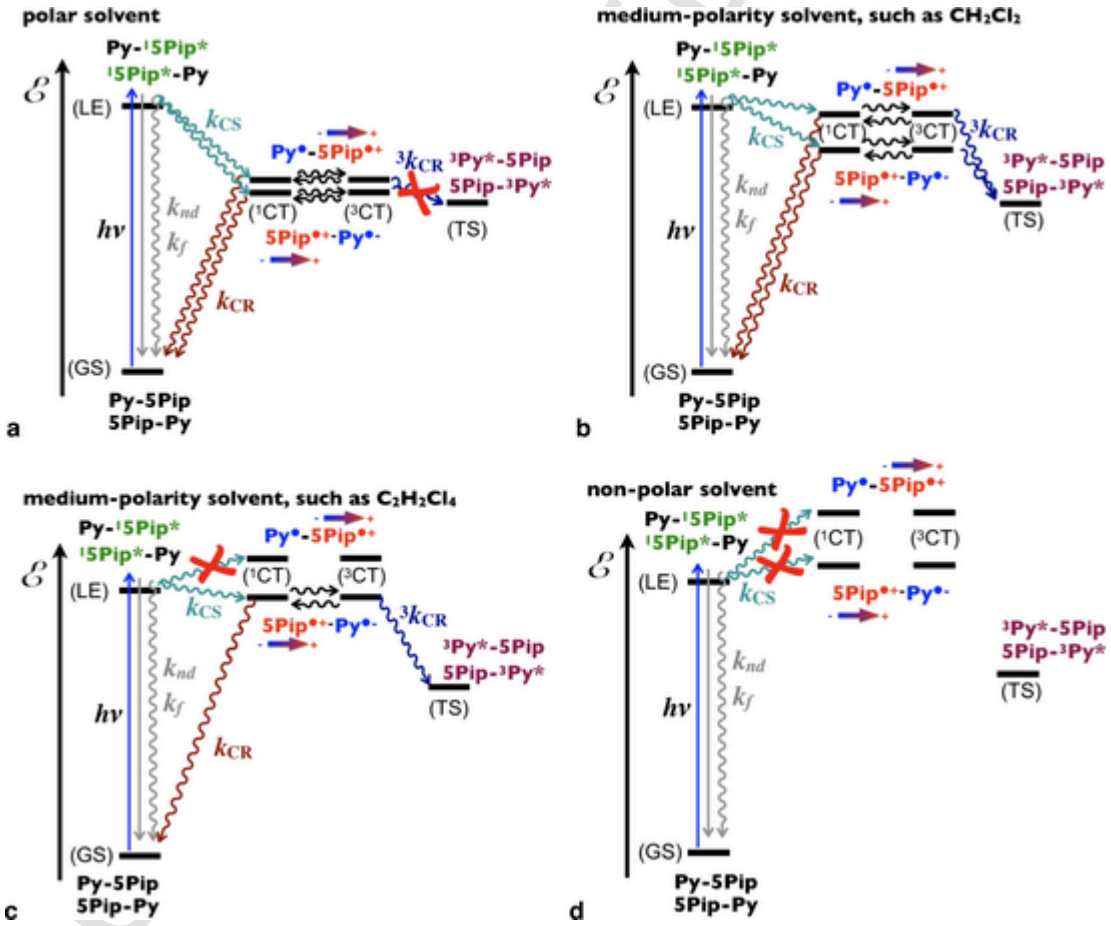


Fig. 3. Jabłoński diagrams for donor–acceptor dyads with the acceptor, Py, linked to the C-terminus (Py-5Pip) and the N-terminus (5Pip-Py) of an anthranilamide residue, 5Pip, which is also the electron donor (Fig. 2) [71]. (a) In polar solvents, the CS and CR rates in both dyads are similar. (b,c) Environment with medium polarity induces the maximum difference between the CT rates of the two dyads, and (c) even suppressing CS in Py-5Pip but not in Py-5Pip. (d) non-polar solvents supress CS in both dyads [71].

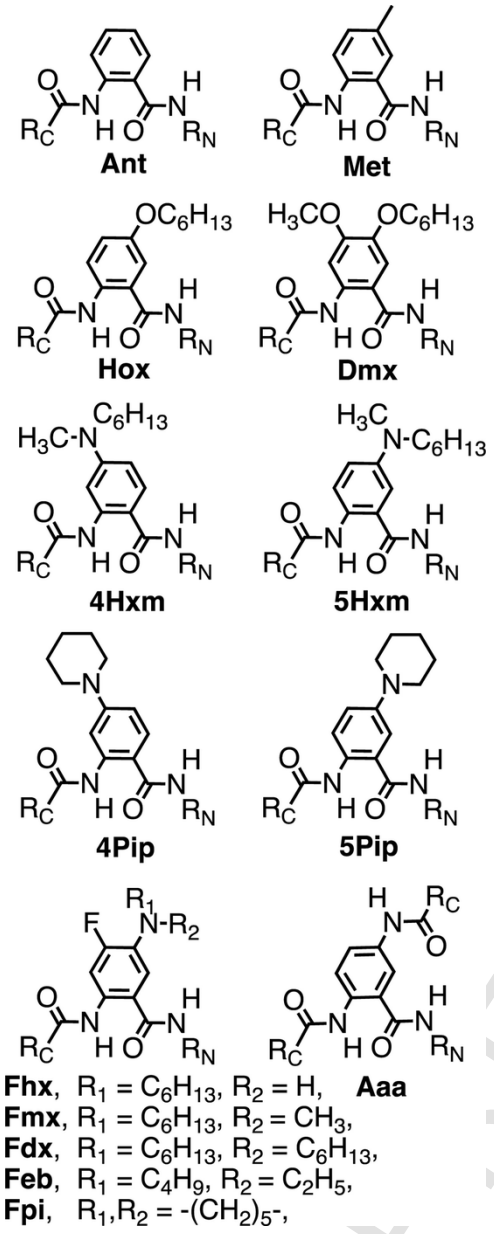


Fig. 4. . Anthranilamide residues for bioinspired molecular electrets [64,66].

istics of the proteins they compose. Each Aa residues can have two side chains (Fig. 4). These side chains are essential for controlling the solubility and aggregation propensities of the Aa structures. In addition, varying the Aa side chains provides an important handle for modifying the electronic and optical properties of these conjugates. That is, a library of Aa residues with different R_1 and R_2 represents a synthetic proteome for structures with countless electronic and photonic functionalities [72].

Our initial focus has been on hole-transfer Aa residues with electron-donating side chains. Varying the electron-donating strength of these R_1 and R_2 groups from amines to alkyls, adjusts the reduction potentials of Aa oxidation over a range of 1 V (Fig. 5) [72–74]. Furthermore, it is important not only what is the side chain, but also at which position it is attached to the aromatic ring of the Aa residue. Shifting an amine from position 4, i.e., R_1 = N(R')R" and R_2 = H, to position 5, i.e., R_1 = H and R_2 = N(R')R", causes about 200 mV negative shift in the reduction potential (Fig. 5) [73].

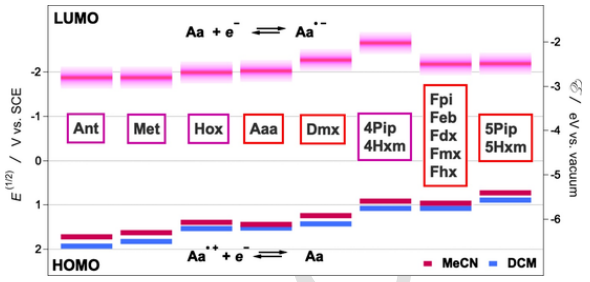


Fig. 5. Reduction potentials and energy levels of the frontier orbitals of Aa residues with different types of electron-donating groups at positions 4 and 5, i.e., R_1 and R_2 (Fig. 1). Fig. 4 shows the structures of the residue and their three-letter abbreviations. The N- and C-termini are capped as alkylamides (Fig. 4) [76].

For pursuing CT via hole hopping mechanism, it is essential for the oxidized residues, $Aa^{\bullet+}$, to manifest reasonable stability. Aliphatic and aromatic amides have notorious propensity for degradation when oxidized at potentials exceeding about 1.4–1.5 V vs. SCE [75], which is an underlying reason why proteins cannot sustainably mediate hole hopping along their backbones. Accordingly, electrochemical oxidation of Aa residues shows chemical irreversibility at high potentials [75]. Keeping the reduction potentials of Aa oxidation under about 1.5 V vs. SCE is a necessary but not sufficient condition for observing reversible behavior. To prevent Aa degradation even at low reduction potentials, the positive charge of the radical ion, defined as its spin density distribution **(SDD)**, should not delocalize over the C-terminal amide [75]. These considerations have become key guidelines for the designs of hole-transfer Aa residues. For example, amines at position 4, i.e., R_1 = N(R')R" and R_2 = H, induce SDD over the C-terminal amide and surely enough results in irreversible oxidation of the Aa residues at about 1.1 V vs. SCE [77]. Conversely, shifting the amine to position 5 and placing and electronegative substituent on position 4, i.e., R_1 = F and R_2 = N(R')R", shifts SDD away from the C-terminal amide that leads to reversible oxidation at the same potential of about 1.1 V vs. SCE [76].

In addition to modulating the electronic properties and the solubility of the Aa residues, the side chains can serve as linker for forming branched oligomers and for ensuring CT pathways with optimal electronic coupling [77]. For hole hopping, the SDD of Aa residues should not extend over their C-terminal amides. Meanwhile, SDD closely resembles the delocalization of the HOMOs, which presents challenges for hole injection through the C-termini (Fig. 5). That is, the electronic coupling with acceptors attached to the C-terminal amides of Aa oligomers is considerably less than optimal. Conversely, electron-donating groups at position 5 shift the delocalization of the radical cation to extend over them and away from the C-terminal amide. Therefore, covalent bonding via side chains at position 5, e.g., R_2 = amide, provides electronic coupling with acceptors that is considerably stronger than linking via the C-terminal amide [77,78].

The diversity of electronic structures that Aa bioinspired molecular electrets makes them a perfect platform for exploring dipole effects not only on CT, but also on electronic and photonic dynamics at different scales.

1.3. Dipole effects on charge transfer

Local electric fields, originating from molecular dipoles, have profound effects on the electronic properties of the microenvironment. As a result, local electric fields from molecular dipoles and ions affect ET, providing a promising means for increasing the efficiency of the desired CT processes while suppressing the undesired ones [71,76–79].

Since the middle of the 20th century, the interest in how electric dipoles affect CT has been growing [21]. It was the 1990s, however, when Boxer showed the role of dielectric asymmetry for the sin-

gle functional pathway for electron transfer in the bacterial photosynthetic reaction center [31]; and Galoppini and Fox reported the first experimental evidence for dipole-induced rectification of long-range CT [80–82]. Using biomimetic polypeptide helices, conjugated with an electron donor and acceptor, they demonstrated the preferential directionality of the photoinduced ET toward the positive pole of the dipole [80–82]. Since these first reports [80–82], the interest in dipole-modulated CT and CTr has been has been steadily increasing through the first two decades of the 21st century [43–46,48,49].

The dipole-generated localized electric fields modulate the electronic properties of the molecular systems in their vicinity. The notion for such effects on CT focusses on dipole-induced changes in the reduction potentials of the donor and the acceptor, $E^{(0)}_{D^{x+n}|D^x}$ and $E^{(0)}_{A^y|A^{y-n}}$, respectively, affecting the driving forces of CT and photoinduced charge transfer **(PCT)** and thus, the Franck-Condon **(FC)** contributions to the CT kinetics [21]:

$$\Delta G^{(0)}_{CT} = F\left(\left(E^{(0)}_{D^{x+n}|D^x} + \phi^{(D)}_{\mu}\right) - \left(E^{(0)}_{A^y|A^{y-n}} + \phi^{(A)}_{\mu}\right)\right) + \Delta G_S + W \quad (1a)$$

$$\Delta G^{(0)}_{PCT} = F\left(\left(E^{(0)}_{D^{x+1}|D^x} + \phi^{(D)}_{\mu}\right) - \left(E^{(0)}_{A^y|A^{y-1}} + \phi^{(A)}_{\mu}\right)\right) + E_{00} + \Delta G_S + W \quad (1b)$$

where $\phi^{(D)}_{\mu}$ and $\phi^{(A)}_{\mu}$ are the dipole-field potentials in the regions of the donor and the acceptor, respectively; W is the Coulombic-work term, representing the interactions between the donor and the acceptor; ΔG_S is the Born-solvation-energy term, representing the interaction of the media with the donor and the acceptor; $\mathscr{E}_{00}$ is the zero-to-zero energy, i.e., optical excitation energy, of the donor or the acceptor; F is the Faraday constant; x and y are the initial charges of the donor and the acceptor, respectively; and n is the number of transferred electrons.

The dipole of even a single electron-rich Aa residue can rectify CT with a pyrene acceptors linked to either its N- or C-terminus [71]. During photoinduced CS, ET along the residue dipole is faster than ET against it, as expected from the field effect on $\Delta G_{PCT}{}^{(0)}$ (eq. 1b) for processes in the Marcus normal region. The kinetic of CR, however, reveals a synergy between the dipole effect on $\Delta G_{CT}{}^{(0)}$ (eq. 1a) and the donor-acceptor electronic coupling [71]. Specifically, the electronic coupling between the CT and the ground state is larger when the acceptor is at the N- rather than at the C-terminus of the Aa residue (Fig. 3) [71]. Concurrently, for CR ET along the dipole is faster than ET against it, which is contrary to the expected effects (eq. 1a) because CS operates in the Marcus inverted region. Decreasing solvent polarity, increases the dipole effect on $\Delta G_{CR}{}^{(0)}$ (Eq. 1a), which suppresses the opposing influence of the donor-acceptor electronic coupling (Fig. 3) [71].

Donor-acceptor conjugates with Aa residues allowed us to demonstrate how to harness the dipole effects on CT, which are inherently enormous [78]. **First**, *media with low polarity enhances the dipole effects on CT* [78]. Lowering solvent polarity destabilizes charged CS states, and not only decreases the CT driving forces, but also can make $\Delta G_{CT}{}^{(0)}$ positive and completely shut down the CT processes. Conversely, decreasing solvent polarity considerably improves the permittivity of the dipole-generated electric fields. As counterintuitive as it may seem, low solvent polarity can substantially increase the rates of ET along the dipole [78]. That is, the dipole effects on CT can exceed the solvation energies of CS states. Concurrently, the same low medium polarity, can completely shut down the ET against the dipole [78].

Second, *placing the donor and the acceptor as close as possible to the solvation cavities of the dipoles is essential for harnessing their effects on CT*. Electric fields from dipoles fall off substantially with distance, e.g., r^{-6} for point-dipole approximation. The Aa electrets present an ideal case where the donor (and the acceptor) can be in the same solvation cavity with the dipoles. Such co-solvation provides an incomparable means for exploring, for example, enhancement of the dipole effects on CT resulting from the Onsager fields. While an increase in the solvent polarity screens the fields outside the solvation cavities of dipoles, the same polarity increase enhances the fields inside dipole solvation cavities [71,79], which has direct implications for the functionalities of solid-state organic materials and devices.

Third, *donor-acceptor systems that inherently have as small as possible CT driving forces in the absence of field are immensely susceptible to dipole effects on the kinetics of CT that they mediate.* When the driving forces are large, relatively small perturbations from the dipole-generated fields can hardly affect the CT kinetics [71,78]. Conversely, when the driving forces are small, dipoles can substantially enhance the CT rates or completely shut down the CS processes.

2. Dipole effects on optical transitions to electronically excited states

The differences in the orientation and the magnitude of the dipole moments of the ground and excited states make spectroscopic transitions susceptible to the presence of external electric fields. This susceptibility is the basis for an effect discovered by Johannes Stark, for which he received the 1919 Nobel Prize in physics [83]. The Stark effect is especially strong for transitions involving excited states with a pronounced CT character [84].

The strength of electric fields in the vicinity of molecular dipoles can reach hundreds of MV m^{-1}, which is quite larger than the average field strengths in 1-cm cuvette with applied external voltage of 1–2 kV, used for Stark spectroscopy [84]. Therefore, molecular electric dipoles can have strong impacts on the spectral properties and the excited-state dynamics of chromophores in their vicinity.

Application of electric fields mainly induces spectral shifts that originate from differences in dipole moments and polarizabilities of the ground and excites sates. Stark spectroscopy involves comparison between spectra of samples in the presence and absence of external electric fields. The measured spectral differences tend to be inherently weak because of the practical limitations on the strength of the applied external electric fields.

Random orientation of chromophores in relevance to externally applied electric, along with inhomogeneities of their microenvironments, presents challenges for interpreting, calculating and predicting experimentally observed Stark effects [84]. Freezing the sample solutions suppresses translational and rotational modes of motion of the sample molecules, which improves the signal to noise ratios. Immobilization of the sample molecules in thin solid films not only suppresses their motion but also can provide a means for attiring some orientation in their arrangement. In general, however, Stark spectroscopy involves measurements of samples with randomized molecular orientation in relevance to the applied external electric fields. Half of the molecules have the dipole-vector differences between the ground and excited states oriented along the applied external field, and the other half – against. Thus, half of the sample molecules cause bathochromic and the other half hipsochromic spectral shifts. Therefore, the differences between the spectra in the presence and absence of external fields, originating from changes in the dipole moment, resemble the second derivative of the spectrum in the absence of field [85].

The field-induced spectral shifts resulting from polarizability changes, however, display different patterns. The induced dipoles, proportional to the polarizability, are always aligned co-directionally with the applied external field. (The direction of electric field is from + to –, while the direction of electric dipoles is from – to + [86]. Hence, the spectral shifts, originating from polarizability changes, will be in the same direction for all molecules in the sample. As a result, the polariz-

ability-induced differences between the spectra in the presence and absence of external fields resemble the first derivative of the spectrum in the absence of field [85].

It is, indeed, trivial to estimate and control the average field strength throughout a capacitance sample cell for optical measurements. Conversely, differences in the dielectric characteristics at micrometer and nanometer scales, involving for example lipid bilayers, live cells, and macromolecules suspended in polar media, can induce significant variations in the field drops in the vicinity of the investigated chromophores, causing them to experience field strengths drastically different from the averaged predictions [84].

Local electric fields, originating from dipoles of moieties that are linked with the photoprobes, offer an attractive alternative. Keeping the linker with the photoprobe short and/or rigid ensures that the orientation of the local electric fields is fixed. When the photoprobe rotates or moves around, the dipole attached to it rotates and moves around the same way. The orientation of the dipole-generated field and the photoprobe are fixed within the frame of the molecule. A strong linker, e.g., covalent or hydrogen bonds, between the dipolar moiety and the probe, subjected to Stark-effect analysis, is essential for keeping the localized electric field fixed. This feature eliminates the need for frizzing the sample or employing other means for immobilization of the probed molecules.

The fixed orientation of the electric fields brings another important consideration for such intramolecular Stark spectroscopy. The vector differences between the dipoles of the ground and excited states of the probe are always oriented in the same direction relevant to the localized field (originating from another neighboring dipole). Therefore, the spectral shifts induced by that localized field (originating from the dipole changes of the probe) are in the same direction for all molecules in the sample. Therefore, differences between the spectra in the presence and absence of the localized electric fields, i.e., dipole-change contribution to the intramolecular Stark effect, resemble the first derivative of the spectrum in the absence of field. This feature is a major difference between Stark spectroscopy and intramolecular Stark spectroscopy.

In comparison with "classical" Stark spectroscopy, intramolecular paradigm allow for attaining drastically larger field effects, and keeping the field orientation fixed. Conversely, keeping the field fixed is also a shortcoming for the intramolecular Stark spectroscopy. The field source is attached to the Stark probe. Hence, the field cannot be turned off or flipped. Any variation in the field strength and orientation requires the synthesis of a new molecule. Despite these challenges, the advantages of intramolecular Stark spectroscopy are overwhelming.

In the 1990s, Lockhart and Kim demonstrated the utility of intramolecular Stark effect for characterization of electric fields originating from the macrodipoles of polypeptide α-helices [87]. A UV absorber with a CT character of its excited state manifests spectral shifts proportional to the field strength at the N-termini of the helices, originating from the macrodipoles [87]. The CT character results in an excited-state dipole that is much larger than the dipole of the ground state. In fact, CT systems are a principal focus of the studies involving Stark spectroscopy. In this case, however, the use of intramolecular Stark spectroscopy was for characterizing the electric fields from the macrodipole of polypeptide α-helices [85].

Electric fields affect transitions between states not only with different dipole moments, but also with differences in their polarizabilities and hyperpolarizabilities [84,88–90]. Pyrene is one of the most widely used organic photoprobes [91], and we have shown its utility for CT studies [93] and for demonstrating dipole effects on CT [71]. Pyrene, along with its alkyl derivatives, does not exhibit solvatochromism [71], which is consistent with negligible differences between the dipoles of its ground and excited states.

Nevertheless, the ground and electronically excited states of pyrene have different polarizability, which dominates the Stark effects that this chromophore exhibits. Applying electric field to pyrene moieties immobilized in polymer films causes bathochromic spectral shifts [92]. In addition, the difference between the pyrene optical spectra in the presence and absence of external field resembles the first derivatives the pyrene spectrum with no field [92]. This finding is consistent with Stark effects originating from polarizability differences [85].

In addition to revealing CT rectification, placing pyrene at the N- and C-termini of an electron-rich Aa residue, 5Pip, induces small spectral shifts that are consistent with an intramolecular Stark effect (Fig. 8). While the absorption spectra of the dyads are roughly the sum of the spectra of the comprising pyrene and 5Pip [71], small shifts of the band maxima contain information about the electronic properties of these conjugates.

When the pyrene is at the N-terminus, the bathochromic shifts in its spectra amount to about 2 nm; and when it is at the C-terminus, they do not exceed 0.5 nm (Fig. 8). These results are consistent with intramolecular Stark effect originating from polarizability differences between the ground and excited states of the pyrene acceptor [92]. These subtle differences in the absorption spectra of the two dyads reveal important features of how the Aa dipole affects the pyrene acceptor. The 5Pip dipole affects the acceptor when it is at the N-terminus stronger than when it is at the C-terminus. While this result suggests that the preferred conformations around the flexible methylene linker place the C-terminal pyrene away from the amide backbone axis, it is consistent with the slight tilt (about 17° toward the aromatic ring, Fig. 2) of the dipole away from the amide back-bone axis, due to the polarization induced by the electron-donating amine at position 5 [71].

Therefore, attaching the electron acceptor to position 5, rather than the N-terminus, of an Aa residue can improve its exposure to the dipole, as dyads comprising an electron-deficient diketopyrrolopyrrole (DPP) may reveal. The absorption bands of DPP are not as sharp as those of pyrene. As a result, the absorption spectra of the DPP dyads with a tri-amide residue, Aaa, overlap almost perfectly (Fig. 9) [79]. The first derivatives of the spectra, however, show that DPP in the dyads with Aaa exhibits about 4-nm hypsochromic shift in comparison with DPP by itself (Fig. 9). Because of the symmetry of DPP, similarly to the pyrene chromophore, differences in the polarizability of the ground and excited states of DPP define the observed intramolecular Stark effects where the directions of the spectral shift does not reflect the dipole orientation. Nevertheless, the magnitudes of the shifts correspond to the strength of the dipole-generated field in the vicinity of the chromophores. This finding demonstrates that a chromophore attached to the N-terminal amide and to the amide at position 5 of the Aaa residue experiences equally strong field effect from the Aaa dipole. It is consistent with the orientation of the Aaa dipole (Fig. 6), and validates the decision to move the chromophore from the C-terminus to the amide at position 5.

While still largely unexplored, intramolecular Stark effects offer an important means for analyzing the electrostatics of molecular, macromolecular, supramolecular and other nanometer-scale structures.

3. How to make molecular electrets?

Computational and experimental studies demonstrated that Aa conjugates possess permanent electric dipoles, i.e., they are molecular electrets [64,70]. Similar to other polypeptides, the chemical synthesis of these Aa electret oligomers proceeds from their C- to their N-termini (Scheme 1). Traditionally, to add every consecutive residue, an amino acid with a protected amine (and protected side-chain groups, if any) and an activated carboxylate is coupled to the free amine at the N-terminus of the oligomer. Selective deprotection of the just-coupled amino acid prepares the oligomer for adding the next residue. This approach is prone to automation, as implemented in solid-phase peptide synthe-

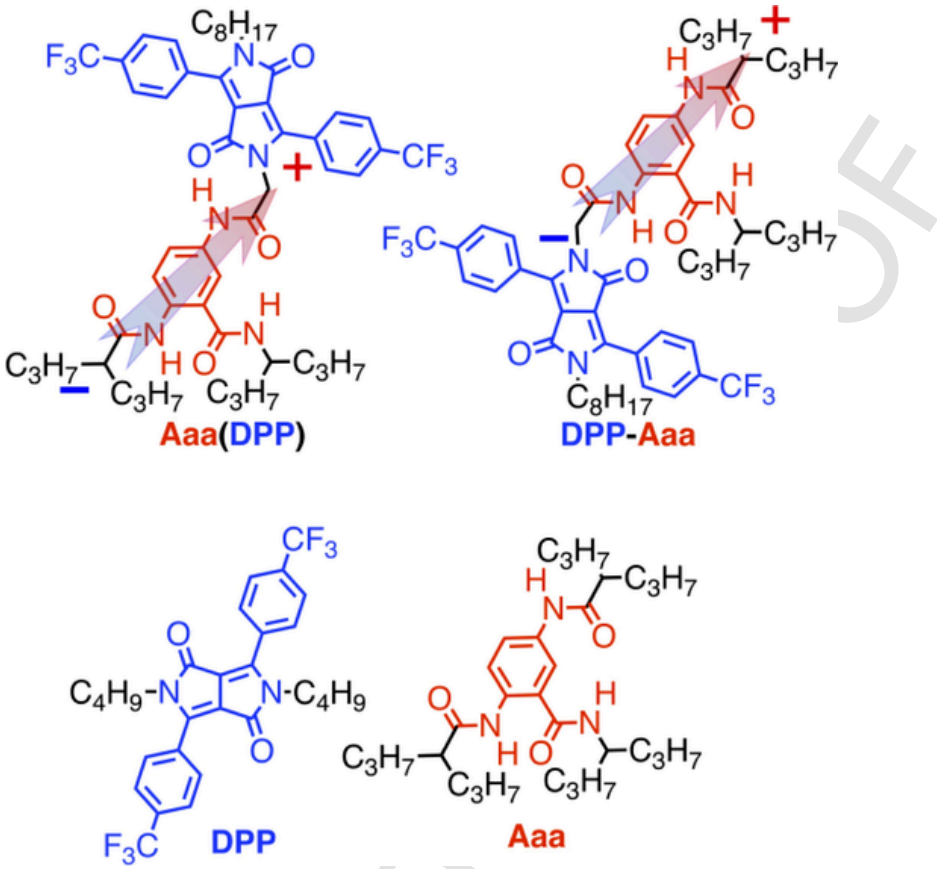


Fig. 6. Donor–acceptor dyads comprising an electron-rich diketopyrrolopyrrole (DPP) as an acceptor linked to the C-terminus (DPP-Aaa) and the side chain (Aaa(DPP)) of an anthranilamide residue, Aaa, which is also the electron donor and a source of an electric dipole. The arrows depict the orientation of the ground-state dipole of Aaa that affects the $S_0 \rightarrow S_1$ transition of DPP. Obtained from multipole expansion, the dipole of the oxidized residue, $Aaa^{\bullet+}$, is larger than that of Aaa and oriented more orthogonally to the Aa axis, i.e., the axis through the N- and C-terminal amides [78].

sis **(SPPS)**. The known protocols for SPPS are robust enough to produce in good yields polypeptides with length exceeding 50 residues.

The bioinspired molecular electrets based on Aa structures are, indeed, polypeptides, composed of aromatic β-amino acids (Fig. 1). Despite all the advances in peptide chemistry, however, none of the established synthetic protocols is applicable for making Aa oligomers because of key structural differences between anthranilic-acid derivatives and the analogues of the native α-amino acids [94].

Why Fmoc-, *t*-Boc- and other established protocols for peptide synthesis fail in the preparation of Aa conjugates? First, the anthranilic residues are considerably less reactive than aliphatic amino acids. The carbonyls at the *ortho*-position decrease the nucleophilicity of the free amines. Similarly, the protected *ortho*-amines decrease the electrophilicity of the carbonyl carbons of the activated carboxylates. Second, activation of carboxyl groups at the *ortho* position to amide or protected amine groups leads to the formation of stable cyclic conjugates. The rigid scaffolding by the aromatic ring places the nitrogen nucleophiles in perfect proximity to the activated carboxylate at the *ortho*-position leading to the formation of lactams comprising four-member rings with quantitative yields (Scheme 2), which we have isolated and characterized using NMR and high-resolution mass spectrometry (HRMS) [94]. This finding deviates from previously reported six-member-ring azlactones that form upon activation of the carboxylates of anthranilic acids [69]. Nevertheless, the four-member-ring lactams, which we observe forming upon activation of anthranilic carboxylates, manifest a pronounced stability. Only strong nucleophiles, such as piperidine, can attack the carbonyl carbon and open the lactam ring [94]. Indeed, these findings render the established methodologies for peptide synthesis impractical and unfeasible for making Aa electret oligomers.

Instead of using anthranilic acids with protected β-amines, introducing each residue as the corresponding derivative of the 2-nitrobenozic acid addresses the grave inherent challenges for making polypeptides based on Aa structures. Specifically, this strategy calls for introducing each β-amine as a nitro group and employing reduction, rather than deprotection, steps [69,72,73,76,77]. Thus, in lieu of the established protocols based on amine deprotection, the building of Aa molecular electrets involves a series of amide-coupling and selective nitro-group-reduction steps (Scheme 1).

Adopting this approach, we have put time and efforts into developing robust methodologies for reliable synthesis of Aa oligomers [94]. Keeping in mind implementation in SPPS that is prone to automation, each of the amide-coupling and nitro-reduction steps has to proceed with quantitative yields and pronounced selectivity under mild conditions in organic media, in which the solid-support resin swells well. In SPPS, the immobilization of the reacting functional groups on the solid support precludes the feasibility of heterogeneous reactions, such as heterogeneous catalysis or preparative electrochemistry, unless organic-soluble molecular shuttles allow for transferring electrons, protons and other species to and from the resin. To prevent permanent contamination of the solid support and blockage of the reaction sites, this latter consideration also renders reagents that form insoluble side products unacceptable.

Keeping these considerations in mind, we have surveyed a wide variety of reactions for amide coupling and nitro reduction and employed them for making Aa derivatives [94]. While the decreased reactivity of the aromatic amines has made the acylchloride amide coupling a preferred route, the search for *in situ* mild activation of the car-

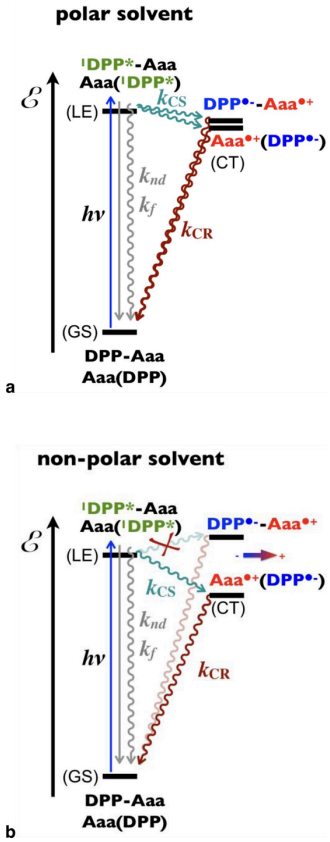


Fig. 7. Jabłoński diagrams for donor–acceptor dyads with the acceptor, DPP, linked to the C-terminus (DPP-Aaa) and the side chain (Aaa(DPP)) of an anthranilamide residue, Aaa, which is also the electron donor (Fig. 6) [78]. (a) Polar media screen the dipoles and the CT states of the two dyads have almost the same energy levels, resulting in small differences between the driving forces and the rates of CS they mediate [78]. (b) Non-polar media enhance the dipole effects, increasing the driving force and the rates of CS mediated by Aaa(DPP), while making $\Delta G_{CS}^{(0)}$ positive for DPP-Aaa, completely suppressing the CT processes [78].

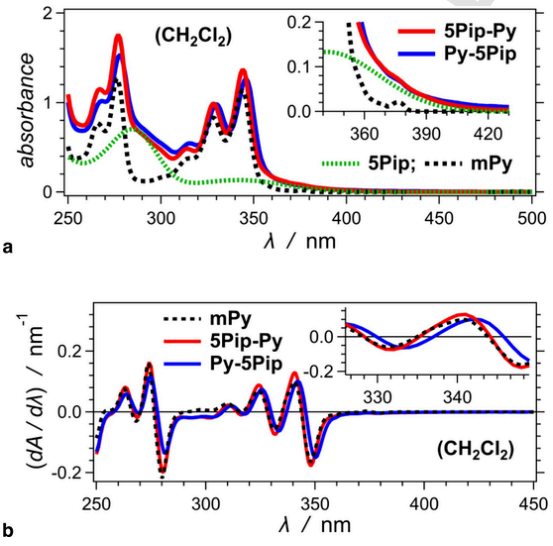


Fig. 8. (a) Absorption spectra of the donor–acceptor dyads, 4Pip-Py and Py-5Pip, along with the spectra of the acceptor, pyrene (Py). An electron-rich anthranilamide residue, 5Pip, is an electron donor and a source of a permanent dipole (Fig. 2) [71]. (b) The first derivatives of the absorption spectra that show clearly the position of the absorption maxima, i.e., at wavelengths for which $dA/d\lambda = 0$.

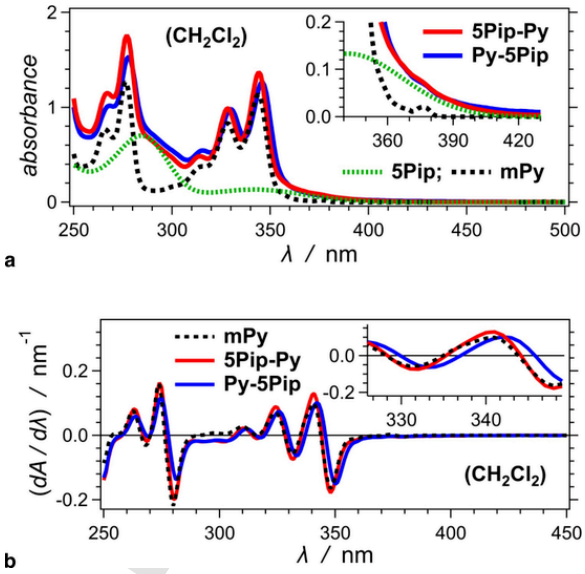
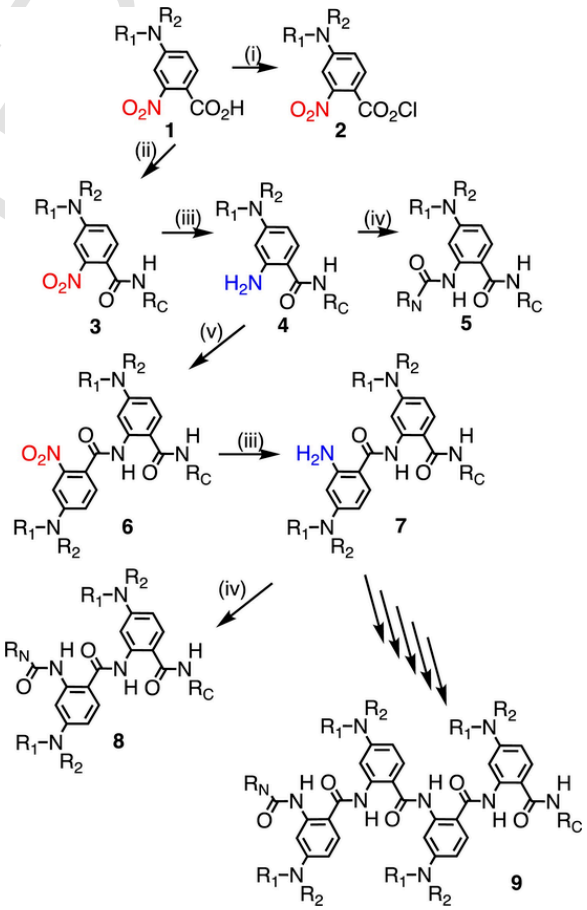
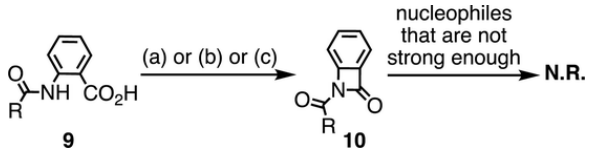


Fig. 9. Absorption spectra of the donor–acceptor dyads, Aaa(DPP) and DPP-Aaa, and the DPP acceptor (Fig. 6) [79]. The first derivatives of the spectra, $dA/d\lambda$ vs. λ, reveal the position of the band maxima, i.e., at the wavelengths where $dA/d\lambda = 0$.



Scheme 1. Example for synthesis of bioinspired molecular electrets. (*i*) $C_2O_2Cl_2$, DCM, 3 drops of DMF, −78 °C (*ii*) DIC, NHS, R_CNH_2, DMF, 0 °C -> r.t. (*iii*) H_2, Pd/C, EtOAc, (*iv*) $(R_NCO)_2O$, pyridine, 40 °C (*v*) **2**, DCM, pyridine, r.t. [94].

boxylic acids to make them susceptible more to amine than to oxygen nucleophiles drives the exploration of other strategies involving, for example, onium salts and carbodiimides. In addition, acylfluorides are orders of magnitude less reactive than acylchlorides. While this decreased re-



Scheme 2. Activation of the carboxylates of Aa residue leads to stable cyclic lactams. (*a*) COCl, DCM, 3 drops of DMF, −78 °C (*b*) EDC, HOBt, NMM, DMF (*c*) TFFH, NMM, DMF (N.R. = no reaction) [94].

activity of the acid fluorides increases the reaction times and may even require convectional or microwave heating, it also makes many undesirable side reactions considerably less probable, which is a principle challenge for reactions involving acylchlorides.

The selective reduction of the nitro groups to amines presents a whole different set of challenges. Exploration of the broad variety of available reduction methods reveals that only a few are appropriate for Aa synthesis and even fewer are potentially implementable in SPPS. Tin (II) chloride is one of the most widely used reagent for selective reduction of nitro groups to amines in different organic solvents, and we have successfully used it in the synthesis of Aa derivatives [71,73]. It requires extensive heating and the tin (IV) side products do not have the needed solubility for washing it away from the reaction mixtures, compromising the overall yields. Despite some reports in the literature of using $SnCl_2$ in SPPS settings, our test reveal that after several reduction steps with tin (II), the side products contaminate the solid support to an extent of bringing the yields to unpractically negligible.

Some of the key challenges for selective nitro reduction involve the synthesis of Aa oligomers requiring conservation of bromide substituents as R_1 or R_2 groups. We determined that dicobalt octacarbonyl, $Co_2(CO)_8$, can selectively reduce nitro groups to amine in high yields after short reaction times [78]. This reaction, however, requires elevated temperatures and some side products from the $Co_2(CO)_8$ oxidation form precipitates in organic media [78].

Our examination of a wide range of nitro-reduction strategies has determined that viologen^{2+}|viologen$^{+\bullet}$and $Cr^{3+}|Cr^{2+}$ organic-soluble redox couples manifest some of the best electrochemical properties for selective reduction of nitro groups in Aa derivatives under mild conditions. While $CrCl_2$ transforms nitro groups to amines with quantitative yields and high electivity at room temperature in organic media, the strict requirements for anoxic conditions when handling $CrCl_2$ are important consideration when developing SPPS methodology.

Presented advances are important steps toward making the bioinspired molecular electrets readily available to wide research and development communities.

4. Conclusions

Bioinspired designs allow for attaining structural features and functionalities beyond what nature offers [95]. Molecular electrets, based on bioinspired Aa structural motifs, have shown their importance not only for understanding dipole effects on CT, but also for developing CT systems of practical importance. Because the Aa electrets are polypeptides (composed of non-native β-amino acid), they offer key venues for bringing principles from proteomics to the design and development of electronic materials and systems. As evident from the perturbations of the optical spectra of chromophores attached to electret residues, intramolecular Stark effects offer a sensitive approach for probing the localized fields originating from molecular dipoles and charges. While still largely unexplored, such effects can serve as important tools for examining the electrostatics of molecular, supramolecular and nanometer-size structures. The intramolecular Stark effects reflect the manners in which dipoles affect optical transitions. The ubiquitous nature of dipoles, and their effects on CT and excited-state dynamics, makes molecular electrets a centerpiece for breakthroughs and advances in electronics, photonics, and energy science and engineering

Authors' statement

VIV conceived the idea for the article and had secured funding for this line of research. KRJ spearheaded the writing of the manuscript, along with VIV. KRJ prepared Figs. 1–7 and the two schemes. VIV prepared Figs. 8 and 9. KRJ conceived the idea for the theme of the journal cover art, and Ms. Joanna Turkowska, from the Institute of Organic Chemistry, Polish Academy of Sciences, Warsaw, prepared it.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Biography

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