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High-performance n-type organic mixed ionic-electronic conductors enabled by strong cation-π interactions

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ABSTRACT

Conjugated polymers that can efficiently transport both ionic and electronic charges have shown broad applications in next-generation optoelectronic, bioelectronic, and energy storage devices. To date, almost all the conjugated polymers have hydrophobic backbones, which impedes efficient ion diffusion/transport in aqueous media. Here, we design and synthesize a novel hydrophilic polymer building block, 4a-azonia-naphthalene (AN). Because of the strong electron-withdrawing ability of AN, the traditional p-type polymer, thiophene diketopyrrolopyrrole (TDPP) polymer, turns into an n-type polymer. More importantly, AN enhances the hydrophilicity and ionic-electronic coupling of the polymer, leading to a fast device response (1.00 ms/0.18 ms) and a high figure-of-merit ($\mu C^*$) of 62.3 F cm$^{-1}$ V$^{-1}$ s$^{-1}$ in organic electrochemical transistor (OECT). We find that cationic aromatics exhibit interesting cation-$\pi$ interactions, leading to smaller $\pi$-$\pi$ stacking distances and interesting ion diffusion behavior. Our work demonstrates that ionic polymer backbones can provide efficient ionic-electronic coupling and charge transport for organic electronics working in aqueous media.
Introduction

Organic materials that can couple ions and holes/electrons transport, also known as organic mixed ionic-electronic conductors (OMIECs), have attracted increasing interest because they are crucial for applications ranging from healthcare, optoelectronic to energy storage applications. Conjugated polymers are soft and flexible materials and thus ideal for biotic interfaces. Meanwhile, conjugated polymers have network-like porous structures, which potentially allow ion diffusion and transport. However, most conjugated polymers with alkyl side chains are hydrophobic, and therefore, ion transport in an aqueous medium is challenging. After introducing ethylene glycol (EG) side chains, conjugated polymers become hydrophilic, making ions and electrons transport much more efficiently in water. The mixed ionic-electronic transport properties of a conjugated polymer are often evaluated by its organic electrochemical transistor (OECT) performance, usually the figure-of-merit, $\mu C^*$ and response time.

Based on the hydrophilic side chain strategy, various p-type polymers have been developed recently, with $\mu C^*$ beyond 200 F cm$^{-1}$ V$^{-1}$ s$^{-1}$. These polymers also exhibit fast response speeds with the $\tau_{on}/\tau_{off}$ less than 1/0.1 ms, good for high-speed sensing applications. However, n-type OECT materials lag far behind. Most n-type OECT materials show $\mu C^*$ values lower than 10 F cm$^{-1}$ V$^{-1}$ s$^{-1}$ with slow response time (usually $\tau_{on}/\tau_{off} > 10$ ms). The poor n-type OECT performance and device stability greatly limit the applications of OECT devices in complementary-like logic circuits and the improvement of the sensitivity of OECT-based biosensors.

To address the low-performance issue in n-type OECT materials, improving both the volumetric capacitance ($C^*$) and electron mobility ($\mu$) are essential. For high-performance p-type OECT polymers, like Poly(3,4-ethylenedioxythiophene) (PEDOT) and Poly(glycolated thiophene-thienothiophene) (p(g2T-TT)), small building blocks (e.g., thiophene) and electron-donating functional groups (e.g., methoxyl- or ether group) are often used. In contrast, to lower the lowest unoccupied molecular orbital (LUMO) energy levels of n-type polymers, large fused heterocyclic aromatics (e.g., naphthalene diimide (NDI), 7,7’-diazaisoindoigo (AIG), bithiophene imide (BTI), pyrazine-flanked diketopyrrolopyrrole (PzDPP),...
benzodifurandione-based oligo(\(\rho\)-phenylene vinylene) (BDOPV)\textsuperscript{29} and electron-withdrawing functional groups (e.g., F or CN) are frequently used. The fused aromatics are large hydrophobic moieties, and the functional groups (F or CN) make the polymer backbone even more hydrophobic\textsuperscript{30}. In addition, traditional electron-withdrawing groups (e.g., F or CN) cannot efficiently lower the LUMO energy levels of the polymers, making electron transport less stable in aqueous environments. Moreover, compared with the simple chemical structure and short synthetic steps of p-type OECT materials, many high-performance n-type OECT polymers have complicated structures and lengthy synthetic steps, which also prevent their practical applications\textsuperscript{26-28}.

Biological systems work in water through various types of intermolecular interactions. For example, ethidium bromide (EB) is often used as the dye for DNA labeling (Fig. 1a)\textsuperscript{31}. Previous studies have demonstrated that the cationic EB molecule can form strong cation-\(\pi\) interactions with nucleotides\textsuperscript{32}. Inspired by the cation-\(\pi\) interactions in biological systems, here we report the design and synthesis of a cationic polymer building block, 4a-azonia-naphthalene (AN, or quinolizin-5-iium) bromide, for n-type OMIECs. The cationic AN exhibits much stronger electron-withdrawing properties than conventional electron-deficient group (e.g., F or CN) functionalized moieties, converting a traditional p-type TDPP-based conjugated polymer to an n-type polymer (Fig. 1d). We find that the AN building block can form strong cation-\(\pi\) interactions with the TDPP moiety, leading to smaller intermolecular \(\pi\)-\(\pi\) distance and extraordinary ion diffusion/injection behaviors in solid state. The cationic building block enhances the hydrophilicity and ionic-electronic coupling efficiency of the polymer backbone, leading to a high OECT performance with \(\mu C^*\) of 62.3 F cm\(^{-1}\) V\(^{-1}\) s\(^{-1}\), fast on/off response times of 1.00 ms/0.18 ms, and improved device stability. These results demonstrate the great potential of using a cationic backbone for high-performance n-type OMIEC materials.
Results and Discussion

**Polymer design and synthesis.** Thiophene-flanked diketopyrrolopyrrole (TDPP) was chosen as the building block for this study because it is cheap and has good charge transport properties due to its planar backbone. However, since the LUMO energy levels of TDPP is relatively high, to date, almost all the TDPP-based conjugated polymers show p-type or ambipolar OECT behaviors. To build an n-type polymer based on TDPP, a copolymerized moiety with a low lying LUMO level is essential. Compared with other naphthalene derivatives, such as quinoline, fluoronaphthalene, and naphthonitrile, 4a-azonia-naphthalene (AN) shows much lower calculated LUMO...
energy levels due to its cationic backbone (Fig. 1c). In addition, we also evaluated the \( \pi-\pi \) interactions between naphthalene (NP), AN and TDPP. The TDPP-AN complex shows larger binding energy (22.1 kcal mol\(^{-1}\)) than the TDPP-NP complex (13.4 kcal mol\(^{-1}\)), which could be attributed to the additional cation-\( \pi \) interactions (Fig. 1b; Supplementary Table 2). To find the optimized structure, we chose seven initial structures, and performed structure optimization. After DFT optimization, five structures with local minimum energy were found (Supplementary Fig. 4). We found that when the bromide ion is close to the hydrogen atoms, the energy is the lowest, which could be due to the hydrogen bonds between the bromide ion and the nearby hydrogen atoms.

The synthesis of AN building block and the polymers are shown in Fig. 2. Ethyl 5-bromopicolinate was reacted with 1,4-butyrolactone via ester condensation, yielding compound 2. Compound 2 has a chiral center but both isomers were reactive in proton-catalyzed decarboxylation-cyclization reaction, yielding compound 3. Compound 3 was dissolved in hydrobromic acid and brominated with liquid bromine. Compound 4 went through a dehydration process, giving AN monomer a good yield. The existence of counterion \( \text{Br}^- \) was evaluated by iontophoresis, and only one major peak (95% area of all anions) was observed (Supplementary Fig. 1), confirming the high purity of the monomer. TDPP was grafted with hepta ethylene glycol methyl ether (mPEG7, \( R_1 \)) and branched ethylene glycol (\( R_2 \)) a the side chains\(^{35,36} \). The branched side chain was employed to further optimize the device performance due to its better hydrophilicity. The di-tributyltin-TDPP was prepared through lithium diisopropyl amide (LDA) deprotonation and SnBu\(_3\)Cl nucleophilic substitution reaction, giving the TDPP tin reagent a purple liquid. The tin reagent was then used immediately for Stille polymerization. The dibromo-AN is soluble in water and common polar solvents. (e.g. DMF). To enhance the polymerization efficiency, we used DMF as the cosolvent for polymerization. The resulting polymer, Poly-4a-Azonia-Naphthalene-thiophene-Diketopyrrolopyrrole with Anion (PANDA) is a dark green solid and is soluble in chloroform. Interestingly, both monomers, the dibromo AN (3) and the TDPP monomer (8), are soluble in water, but the polymer PANDA is not water-soluble, suggesting the
strong intermolecular interactions between the repeating units (Supplementary Fig. 2). For comparison, we also synthesized an isoelectronic polymer, Poly-NaPhthalene-thiophene-Diketoxylopyrrole (PNPD), which has an almost identical backbone except for one atom. The molecular weight of both polymers was evaluated by gel permeation chromatography (GPC). All the polymers showed high molecular weights with $M_n$ in the range of 25.1~46.4 kg mol$^{-1}$ and PDI in the range of 1.51~1.76. We also carried out thermogravimetric analysis, due to the evaporation of bromide ions, PANDA and PANDA2 showed relatively lower degradation temperatures than PNPD (Supplementary Fig. 3).

 Density functional theory (DFT) study shows that PANDA has a more planar backbone conformation; while PNPD has a larger dihedral angle (Fig. 1e). To understand this difference, we carried out a relaxed potential energy surface (PES) scan of the torsional angles between the TDPP and AN/NP moieties. As shown in Fig. 1e and Fig. 1g, TDPP-AN has a rotational barrier as high as 11 kcal mol$^{-1}$; while for TDPP-
NP, the barrier is only 3 kcal mol\(^{-1}\). To our knowledge, such a high rotational barrier is seldomly observed in conjugated polymers. Further theoretical analysis suggests that the high rotation barrier is largely due to the strong electron-withdrawing property of AN, making more electrons originally on thiophene distribute onto AN moiety (Supplementary Fig. 9). This charge redistribution could shorten the bond length between thiophene and AN (Fig. 1g) The bond length of TDPP and AN unit is 1.44 Å, between a typical single bond and a double bond (see more detailed analysis in Supplementary Figs 7, 8 and 9). We also used Mayer bond order analysis to explain the planarity of PANDA. We find the bond between naphthalene and DPP is 1.0 and the bond order between AN and DPP is 1.2, confirming the stronger \(\pi\)-bond feature of the TDPP-AN bond (Fig. 10). In addition, the HOMO of PANDA is localized on the TDPP moiety, whereas the LUMO is delocalized along the polymer chains (Fig. 1d, here we omitted the orbitals on the \(\text{Br}^-\)). Compared with PANDA, both the frontier orbitals of PNPD are delocalized (Supplementary Fig. 6). These results suggest that cationic building blocks could bring new molecular features (e.g. better backbone planarity, higher rotational barrier, and different frontier orbital distributions) rather than simply lowering LUMO energy levels.

**Electrochemical Properties and OECT Device Performance.** We measured the UV-vis spectra of PANDA and PNPD to understand their electronic properties (Fig. 3a and Fig. 3d). The absorption onset of PANDA is 979 nm in solution, and 1076 nm in solid state (Fig. 3a). After going from solution to solid state, both polymers showed redshifted spectra which is due to the polymer aggregation in the solid state. Compared with PNPD (Fig. 3d, 778 nm to 931 nm), the shift of PANDA is smaller, suggesting that PANDA has a more planar backbone conformation in solution. This is supported by the above DFT calculations that the rotational barrier between AN and TDPP is higher than NP and TDPP, and the most stable conformation of TDPP-AN is at 0.8°. Thus, AN provides PANDA with a more planar and rigid backbone, which will benefit intrachain and interchain charge transport. We also performed detailed theoretical spectra calculation in Supplementary Figs 11, 12 and 13.
The redox properties of the two polymers were measured by cyclic voltammetry (CV). The measured LUMO energy level of PANDA (−4.21 eV) is much lower than that of PNPD (−3.78 eV), consistent with the DFT calculations (Supplementary Table 1). Compared with other TDPP-based polymers, PANDA has the lowest LUMO energy level. Continuous CV sweeps of two polymers were explored in 0.1 M NaCl solution. Both PANDA and PNPD show good stability in the cycling test with small current decay (Supplementary Fig. 15). To investigate the electrochemical characteristics of both polymers, spectrochemistry was performed. PANDA is electrochemically doped since bias at −0.3 V and fully doped at −0.8 V, while PNPD is not completely doped even at +1 V (Fig. 3b and Fig. 3e). This indicates that PANDA can be readily reduced and is a typical n-type material, while PNPD is a p-type material. The polaron peaks of both polymers raised and the original peak decreased, exhibiting a typical electrochemically doping process. The polaron peak of PANDA (>1000 nm) is much stronger than that of PNPD (> 800 nm), suggesting that PANDA can be readily reduced. These results imply that PANDA could exhibit satisfactory n-type OECT performances.

The OECT devices of both polymers were fabricated using a photolithography and parylene-patterning method. The polymers were deposited using their chloroform solutions. The performances of the OECT devices were evaluated using the following Bernards’ model:

\[ g_m = (W / L) \cdot d \cdot \mu \cdot C^* |(V_{th} - V_{GS})| \]

where \( W, L, \) and \( d \) are the channel width, length, and film thickness, respectively; \( \mu \) and \( C^* \) donate the charge carrier mobility and the volumetric capacitance; \( V_{th} \) and \( V_{GS} \) are the threshold voltage and gate voltage.

PNPD shows a typical p-type OECT performance with a low \( \mu C^* \) of 0.262 F cm\(^{-1}\) V\(^{-1}\) s\(^{-1}\), which is probably due to its non-planar backbone and high oxidation potential. In comparison, PANDA shows n-type OECT behaviors as we expected. The introduction of cationic fragments effectively lowers the LUMO level and switches a p-type polymer to an n-type one. The normalized transconductance \( (g_{m,norm}) \) of PANDA is 14.7 S cm\(^{-1}\) and the calculated \( \mu C^* \) is of up to 40.7 F cm\(^{-1}\) V\(^{-1}\) s\(^{-1}\). For PANDA with branched EG chains, \( g_{m,norm} \) reaches 19.3 S cm\(^{-1}\) and \( \mu C^* \) reaches 62.3 F cm\(^{-1}\) V\(^{-1}\)
s\(^{-1}\) (Fig. 3c; Supplementary Table 4). To our knowledge, these values are among the highest in n-type OECT materials. A high-performance p-type polymer P(bgDPP-MeOT2)\(^{35}\) was employed to fabricate complementary inverters with PANDA. When the supply voltage \((V_{DD})\) is set to 0.5 V and the input voltage \((V_{in})\) is swept from 0 to 0.5 V, a record high gain value \((\partial V_{out}/\partial V_{in})\) of 71 at 0.5 V is obtained (Supplementary Table 7). The inverter also shows very small hysteresis and rail-to-rail voltage swings. The inverter performance is already comparable to the OECT-based inverters employing inorganic IGZO as the n-channel material\(^{41}\).

We measured the capacitance of the OECT device by electrochemical impedance spectroscopy (EIS) and found that the \(C^*\) is 181 F cm\(^{-3}\) for PANDA and 197 F cm\(^{-3}\) for PANDA2 (Supplementary Fig. 18). The high capacitances indicate the good ion diffusion and penetration in these polymers. The mobilities are calculated to be 0.23 and 0.33 cm\(^2\) V\(^{-1}\) s\(^{-1}\) for PANDA and PANDA2, respectively. PANDA also shows fast response speed of \(\tau_{on}/\tau_{off} = 2.34/0.30\) ms, and PANDA2 shows even faster response speed of \(\tau_{on}/\tau_{off} = 1.00/0.18\) ms (Fig. 3g), which is the fastest value in donor-acceptor n-type OECT polymers (Fig. 3i and Supplementary Table 4)\(^{20,21,26,27,34,42}\). We relate the high response speed to its hydrophilic cationic backbones and high electron mobility. The hydrophilic backbone allows fast ion diffusions, and the high electron mobility guarantees fast charge transport between source-drain electrodes. Thus, PANDA is a promising material for real-time high-speed sensing applications. PANDA also shows high stability under on-off cycling with current retention of 89% after 2500 s operation in air (Fig. 3h)\(^{43,44}\). This is higher than the current state-of-the-art n-type materials, such as f-BTI2g-TVTCN (75% current retention after 2400 s cycling) and P(gTDPP2FT) (61% retention after 2500 s cycling)\(^{27,36}\). In comparison, PNPD shows poor operation stability, probably due to its low HOMO energy level, making the polymer cannot be easily oxidized (Supplementary Fig. 22). Therefore, the cationic hydrophilic fragment improves the volumetric capacitance and the strong cation-\(\pi\) interaction of AN enables high charge carrier mobility under doped conditions. All the features endow PANDA with high mixed ionic-electronic coupling efficiency and thereby better OECT device performances. To explore the generality of incorporating AN for other polymers, we
performed DFT calculations for other promising AN-based polymers. After incorporating AN, all the polymers show significantly lowered LUMO levels in the range of $-3.61$ to $-4.24$ eV. The LUMO levels lowered by $0.47$–$1.71$ eV due to AN’s strong electron deficiency. Therefore, AN can greatly lower the LUMO levels of conjugated polymers and might be a general choice for converting p-type conjugated polymers to n-type (Supplementary Fig. 29 and related discussions).

Table 1 | Summary of the OECT performance of the two polymers.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>$g_m$ norm</th>
<th>$V_{th}$</th>
<th>$\mu C^c$</th>
<th>$\mu^d$</th>
<th>$C^*$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PANDA</td>
<td>14.7</td>
<td>0.44</td>
<td>40.7 (39.6 ± 1.6)</td>
<td>0.23</td>
<td>181 ± 19</td>
</tr>
<tr>
<td>PANDA2</td>
<td>19.2</td>
<td>0.47</td>
<td>62.3 (51.4 ± 6.8)</td>
<td>0.33</td>
<td>197 ± 8</td>
</tr>
<tr>
<td>PNPD</td>
<td>0.0445</td>
<td>$-0.67$</td>
<td>0.262 (0.232 ± 0.022)</td>
<td>0.0019</td>
<td>137 ± 26</td>
</tr>
</tbody>
</table>

$^a$The W/L of all devices is 100/10 μm. All of the OECT devices were operated in a 0.1 M NaCl aqueous solution. $^b$$V_{th}$ was determined by extrapolating the corresponding $I_{DS1/2}$ versus $V_{GS}$ plots. $^c$The data outside the brackets are maximal data, and the inside ones are the average. $^d$μ was calculated from $\mu C^*$ and the measured volumetric capacitance $C^*$. PNPD is a p-type polymer. Several devices were tested and computed for each polymer (see details in Supplementary Table 5).
**Fig. 3** Polymer properties and OECT device characterization. (a) and (b) Absorption spectra and electrochemical spectra of PANDA. (c) Transfer characteristics of PANDA2. $V_{DS} = 0.6$ V, $W/L = 100/10$ μm. (d) and (e) Absorption spectra and electrochemical spectra of PNPD. (f) Voltage transfer characteristics and gain of the complementary inverter based on PANDA and P(bgDPP-MeOT2). (g) Transient response of PANDA2. (h) Long-term on-off switching of PANDA. $V_{DS} = 0.6$ V; a gate voltage pulse $V_{GS} = 0.8$ V; $W/L = 100/10$ μm. (i) Comparison of the response time ($\tau$) and $\mu C^*$ for current state-of-the-art n-type OECT polymers.

**Film microstructure characterization.** Grazing incidence wide-angle X-ray scattering (GIWAXS) and atomic force microscope (AFM) were employed to explore the molecular packing and film morphology. PANDA shows a face-on molecular packing, while PNPD shows an edge-on packing (Fig. 4a and Fig. 4b). The lamellar distance of PANDA is 30.1 Å, larger than that of PNPD (24.2 Å). The larger lamellar distance might correspond to the bromide counterions inserted into the glycol side chains. Notably, PANDA has a $\pi-\pi$ stacking distance of 3.59 Å, shorter than that of PNPD (3.65 Å), which could be attributed to the cation-$\pi$ interaction in PANDA. This change suggests a stronger interchain interactions. Compared to PNPD, PANDA has a smaller persistent length and larger paracrystalline disorder ($g$ value) (Supplementary Table 3), suggesting that PANDA has lower crystallinity and poor molecular order in solid state. The lower crystallinity of PANDA is probably due to the interference of the bromide counterions (Supplementary Table 3). We also measured the GIWAXS of the polymer film after being exposed to aqueous media and electrochemically doped. The scattering of PANDA film showed no obvious change after being exposed to the electrolyte. After being reduced, the $\pi-\pi$ stacking peak (010) becomes stronger and the $\pi-\pi$ stacking distance becomes smaller (3.59 Å to 3.51 Å), suggesting that the molecular packing of PANDA becomes a little bit more ordered with even smaller interchain distance (Fig. 4c). In contrast, after being exposed and oxidized, the scattering of the PNPD film showed weaker lamellar and the $\pi-\pi$ stacking distance becomes larger (3.65 Å to 3.66 Å) (Fig. 4d). Both polymer films are smooth with small root-mean-square (RMS) roughness in AFM height images (Supplementary Fig. 23). PANDA has fiber-like networks with smaller grain sizes than PNPD, consistent with the smaller persistent
length of PANDA. After being exposed to water and electrochemical doping, both polymers show small morphological changes, and the roughness of the films is slightly improved. All these results seem to contradict the good charge transport property of PANDA since polymers with higher crystallinity often exhibit better charge transport properties\textsuperscript{46}. However, recent studies have shown that molecular packing order is not the most important parameter for high-mobility conjugated polymers, and good intrachain charge transport and interchain short-range contacts are more critical\textsuperscript{47,48}. PANDA has a more planar backbone and a smaller $\pi$-$\pi$ stacking distance. Its planar backbone allows faster intrachain transport, and the smaller $\pi$-$\pi$ stacking distance guarantees efficient interchain charge transport. Both features originate from its cationic backbone.

![Molecular packing and morphology characterization](image)

**Fig. 4** Molecular packing and morphology characterization. (a) and (b) 2D-GIWAXS of PANDA and PNPD in their pristine films. (c) and (d) Line cuts along the $q_{xy}$ direction represent scattering in the in-plane direction, while the $q_z$ is from the out-of-plane direction. “Pristine” stands for dry films without any treatment. “Exposed” stands for the films immersed in 0.1 M NaCl for 10 min and blow-dried. “Oxidized/Reduced” stands for the films on the silicon substrate that are oxidized/reduced by voltage bias for 10 min and blow-dried.
To further understand the film changes after exposed to electrolyte and doping, we performed electrochemical quartz crystal microbalance with dissipation (EQCM-D) measurements. We found that PANDA showed interesting water absorption and ion diffusion/injection characteristics (Supplementary Fig. 24). PNPD showed passive swelling of 61.4% (exposed to 0.1 M NaCl), and an active swelling of 6.3% (electrically biased at +0.9 V vs. Ag/AgCl). An n-type polymer P(gTDPP2FT) exhibited passive swelling of 113%, and an active swelling (biased at −0.9 V) of 1.3%\(^36\). However, PANDA showed huge passive swelling of 153%, but no obvious active swelling (biased at −0.8 V). We propose that the unique swelling characteristics of PANDA result from its cationic structure. The Na\(^+\)·xH\(_2\)O will penetrate into the film, while the Br\(^−\)·yH\(_2\)O will go out at the same time. The mass changes are just in balance that EQCM-D shows no net mass change. However, for polymers with a neutral backbone (for both p- and n-type polymers), there must be an obvious mass change during oxidation/reduction, which could lead to instability of the devices\(^49\).

Understanding of the cation-\(\pi\) interactions. OECTs are usually operated in aquatic environment, so we studied AN and TDPP interactions in D\(_2\)O using solution \(^1\)H NMR. TDPP is dissolved in D\(_2\)O at a concentration of 16.2 mM. By increasing the AN from 0 to 18.6 mM, we observed clear changes in the chemical shift of all the H on TDPP. Among them, H\(_a\) and H\(_b\) shifted to a lower field (higher radiation frequency, Hz), whereas H\(_c\) shifted to a higher field (lower frequency) (Fig. 5b). This indicates that H\(_c\) is strongly shielded by AN while the other two H on thiophene are deshielded. To exclude the potential effects caused by anions, we added tetra-\(n\)-butylammonium bromide (Bu\(_4\)N\(^+\)Br\(^−\)) to the TDPP solution. As shown in Fig. 5c, we only observed slightly deshielding effects caused by the Br\(^−\), which may originate from the weak Br\(^−\)…H interactions. Control experiments also show that salts with different anions have weak effects on the NMR spectra (Supplementary Fig. 25). Thus, the large chemical shifts are caused by the cations, not by the anions. This shielding and deshielding effect can be well understood by our optimized AN-TDPP molecular packing model (Fig. 5a).
When AN is on top of TDPP, H_c is under AN, leading to shielding effect; while H_a and H_b are outside of the AN covered area, resulting deshielding effect.

We also carried out temperature-variable $^1$H NMR experiments (Fig. 5d). For TDPP in water, we found that new peaks start to appear above 70 °C, which can be attributed to the aggregation of the TDPP (Supplementary Fig. 26). Since higher temperature can destroy the hydrogen bonds between the EG side chains and water$^{50}$, the solubility of TDPP starts to decrease and result in aggregates formation (Fig. 5d, TDPP at 90 °C, blue circle). After adding AN to the TDPP solution (1:1 molar ratio) and raising the temperature above 70 °C, except for the TDPP aggregates’ peaks, a new set of peaks appeared, which can be attributed to the AN-TDPP complex. The new peaks are broadened, suggesting that the AN-TDPP might adopt different packing conformations. After cooling to room temperature (RT), the AN-TDPP formed some precipitates, further confirming the formation of the AN-TDPP complex (Fig. 5d, blue circle). All the above results demonstrate that the cationic AN indeed forms strong cation-π interactions with TDPP in water, which well explains the short π-π stacking distance in film and the poor solubility of PANDA in water though both monomers are soluble.

To explore the cation-π interactions in solid state, we performed the solid-state NMR using $^{13}$C high-power decoupling with magic angle spinning (HPDec-MAS) technique for the monomers (Supplementary Fig. 28). The HPDec-MAS experiment excites all nuclei non-selectively and the integration of the peak is related to the carbon content. All samples are dispersed in inertia silica, and the chemical shifts (δ ppm) were determined to an internal standard. With the addition of AN to DPP, the peaks in the range of 120–140 ppm raised dramatically, while the peaks between 55 ppm and 78 ppm remain the same as the DPP monomer. When mixed with DPP, the peak of AN at 110 ppm disappear and most of the AN peaks shifted clearly. Combining all the data, we can conclude that DPP has a strong interaction with AN in solid state. The shielding effect of the DPP caused the disappear and the shift of the C atoms on AN and these effects happened only on the aromatic core due to the cation-π interactions, since the C atoms of the side chains are less affected.
Fig. 5 | Understanding of the cation-π interactions between TDPP and AN. (a) TDPP structure and the optimized molecular packing model of AN-TDPP complex. (b) Chemical shift changes of TDPP after adding 0, 2.43, 4.54, 5.67, 8.42, 10.7, 16.5, 18.6 mM AN in D$_2$O, the concentration of TDPP is 16.2 mM. (c) Chemical shift changes of TDPP after adding 0 to 100 mM TBAB in D$_2$O. See the full concentration range in Fig. S15. The TDPP concentration is also 16.2 mM. (d) The phase separation of TDPP solution during heating. TDDP, AN, and TDPP+AN show good solubility in water at RT. TDPP forms a drop of oil at 90 °C, suggesting the aggregation of TDPP. TDPP+AN forms amorphous precipitates at 90 °C. AN solution is clear at 90 °C. (e) Variable-temperature (VT) $^1$H-NMR of TDPP and AN mixture (1:1 molar ratio).

Discussion

In summary, we have developed a cationic building block, namely AN, for n-type OMIECs. AN has a simple structure but with unprecedentedly strong electron-withdrawing properties and successfully converts a p-type polymer to a high-performance n-type OMIEC. We found that water-soluble cationic AN can form strong π-π stacking interactions with water-soluble TDPP via cation-π interactions. The strong underwater cation-π interactions physically cross-linked the polymer, making it insoluble in water and leading to a shorter π-π stacking distance and high electron mobility in the solid state. In addition, the cationic backbone also enhances hydrophilicity, leading to high volumetric capacitance and fast ion diffusion/injection. All these features enable the polymer, PANDA2, with a high normalized
transconductance ($g_{m,norm}$) of 19.3 S cm$^{-1}$, $\mu C^*$ of 62.3 F cm$^{-1}$ V$^{-1}$ s$^{-1}$, and fast response speed of 1.00 ms/0.18 ms. Meanwhile, the stronger cation-$\pi$ interactions endow the polymer with interesting ion diffusion/injection features and high operational stability. Different from conventional polymer design focusing on the synthesis of polymers with neutral backbones, our work demonstrates a new approach using ionic backbones for next-generation organic electronic materials working in aqueous media.

**Data availability**

The authors declare that the data supporting the findings of this study are available within the paper and its Supplementary Information files. Source data are provided in this paper.

**Reference**


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**Author contributions**

Z.H. and P.L. contributed equally to this work. Z.H. and X.P. synthesized and characterized the polymers. Z.H., Y.L. and X.D. performed computational study. P.L. and Y.L. performed device fabrication and characterization. Y.C. performed the electrophoresis characterization. Z.H., P.L., J.Y.W. and T.L. wrote the manuscript. All authors revised and approved the manuscript.

**Competing interests**
The authors declare no competing financial or non-financial interests.

Additional information

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