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Cation-Dependent Mixed Ionic-Electronic Transport in a Perylenediimide Small-Molecule Semiconductor

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Abstract: A rapidly growing interest in organic bioelectronic applications has spurred the development of a wide variety of organic mixed ionic-electronic conductors. While these new mixed conductors have enabled the community to interface organic electronics with biological systems and efficiently transduce biological signals (ions) into electronic signals, the current materials selection does not offer sufficient selectivity towards specific ions of biological relevance without the use of auxiliary components such as ion-selective membranes. Here, we present the molecular design of an n-type (electron-transporting) perylene diimide semiconductor material decorated with pendant oligoether groups to facilitate interactions with cations such as Na⁺ and K⁺. Using the cyclic 15-crown-5 oligoether motif, we find that the resulting mixed conductor **PDI-crown** displays a strong dependence on the size of the electrolyte cation when tested in an organic electrochemical transistor configuration. In stark contrast to the low current response on the order of 1 μ A observed with aqueous sodium chloride, a nearly 200-fold increase in current is observed with aqueous potassium chloride. We ascribe the high selectivity to extended molecular aggregation and therefore efficient charge transport in the presence of K⁺ due to a favourable sandwich-like structure between two adjacent 15-crown-5 motifs and the potassium ion.

Over the last decade, organic mixed ionic-electronic conductors (OMIECs) have developed rapidly due to their ability to provide efficient ionic and electronic charge transport and storage of relevance for a variety of bioelectronic applications.^[1,2] OMIECs are typically solution-processable, amenable to facile chemical modification and with high biocompatibility, which has paved the way for numerous groundbreaking bioelectronic devices, such as neuro-morphic devices,^[3,4] cortisol^[5] and epinephrine sensors,^[6] glucose^[7] and lactate detectors,^[8] which make use of the organic electrochemical transistor (OECT) as an efficient amplifying transducer of biological (ionic) signals into electronic signals.^[9-12]

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Exploring the molecular design requirements and considerations of the OMIEC materials is crucial. Chemical modification at the molecular level will ultimately determine the performance of the corresponding device. From the literature, some general design principles can be extracted.^[13-15] Backbone planarity, for example, is a prerequisite to obtain tight π -stacking and good electronic charge transport.^[16,17] Side chain engineering is another consideration with side chains containing oligoethylene glycol, sulfonate, and crown ether moieties found to impact ion injection and transport in the bulk material, as well as balance solubility considerations with backbone packing.^[18-20]

Crown ethers are heterocyclic compounds comprising multiple repeating ethyleneoxy units. They are widely recognised for their ability to bind various cations selectively, controlled by matching the radii and charge density of the cations with the cavity radius of the crown ether (Figure 1a). For example, 15-crown-5 with the cavity radius of 0.86–0.92 Å has a high affinity for the sodium cation (Na⁺) with an ionic radius of 1.02 Å.^[21,22] Typically, when the cation is larger than the cavity radius of the crown ether, the complexes have strong tendency to form sandwich-like structures, in which the cation lies between two crown ether units (Figure 1b).^[23–25]

Considering the fact that Na⁺ and potassium ions (K⁺) stand out as two prevalent cations that play crucial roles in various biological activities including regulation of blood pressure and metabolic transport,^[26] OECTs that display selectivity towards Na⁺ or K⁺ are of significant interest. Sessolo et al. integrated a polyvinylchloride-based ionselective membrane with an OECT channel to achieve a

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Figure 1. a) Schematic illustration comparing crown ether cavity radius with effective ion radii of selected alkali metals; b) schematic illustration of 15-crown-5: metal ion complexes of varying stoichiometry; c) synthetic routes for the preparation of PDI-PEG and PDI-crown.

selective response to K⁺.^[27] Keene et al. reported a solidstate wearable OECT patch with ammonium and calcium ion-selective membranes, which can detect the physiological concentration of the relevant cations.^[28] Analogously, a sodium-selective OECT was fabricated by Han et al. using an ion-selective membrane to detect ions with fast response times.^[29] Contrasting the membrane approach, a few examples of single component conjugated polymers functionalised with crown ether moieties have also been reported.^[30,31] Inal et al. demonstrated a moderately selective electrical response to Na⁺ and K⁺ ions upon coating an OECT gate with crown ether functionalised polythiophenes.^[30] With a lack of solubility, these materials are restricted to electrodeposition, while solution-processable ion-selective organic semiconductors have only shown ion-selective optical responses and not been incorporated in OECTs so far.[32-35]

Here in this work, we designed two solution-processable perylene diimide based small molecules; PDI-crown bearing 15-crown-5 motifs and PDI-PEG bearing linear pentaethylene glycol chains, which are employed as channel materials in OECT devices. Pervlene diimide (PDI) is characterised by a large coplanar structure, high electron affinity and favourable charge carrier transport, making it a popular electron-accepting building block for the construction of ntype (electron-transporting) semiconducting materials.^[36-38] The hydrophilic oligoether motifs (linear or cyclic) appended on the imide nitrogen facilitate ionic transport while the distinctive binding properties of 15-crown-5 in PDIcrown enable the selectivity for specific alkali metal ions. Specifically, we show that the sandwich-like structure of the **PDI-crown**: K⁺ complex leads to tight intermolecular packing and good long-range electronic transport evidenced by OECT devices with PDI-crown active layers that show two orders of magnitude differences in current depending on the choice of electrolyte cation (Na⁺ versus K⁺).

The synthetic routes for the preparation of **PDI-crown** and **PDI-PEG** are shown in Figure 1c. Both molecules can be prepared by a one-step imidization reaction.^[39] **PDI-crown** was obtained in 80% yield by reacting perylene-3,4,9,10-tetracarboxylic dianhydride and 2-aminomethyl-15-

crown-5 at 170 °C in dimethylformamide. The pentaethylene glycol amine was similarly reacted with perylene-3,4,9,10-tetracarboxylic dianhydride to afford **PDI-PEG** in a yield of 66 %. The chemical structures of the **PDI** small molecules were confirmed using ¹H NMR, ¹³C NMR spectroscopy, and high-resolution mass spectrometry. Both compounds possess good solubility in common organic solvents, such as dichloromethane and chloroform at room temperature. Thermogravimetric analysis (Figure S9) indicated high thermal stability with 5 % weight loss at 370 °C for **PDI-Crown** and 369 °C for **PDI-PEG**. Differential scanning calorimetry (Figure S10) revealed several thermal transitions for **PDI-PEG** whereas an amorphous solid was inferred for **PDI-rown** as no thermal transitions were observed.

The UV/Vis absorption spectra of **PDI-PEG** and **PDIcrown** in chloroform solution are shown in Figure 2a. The two compounds exhibit similar spectra extending from 400 to 550 nm with three pronounced peaks at 458, 490 and 526 nm. The near-identical spectra indicate that the imide substituent has a negligible influence on the electronic properties of the central building block. This is further corroborated by the highly similar cyclic voltammograms for the two compounds when probed in dichloromethane solution with tetrabutylammonium hexafluorophosphate (TBAPF₆) as the supporting electrolyte (Figure 2d).

To investigate possible interactions between the **PDIcrown** and alkali metal ions, absorption and emission spectroscopy titration experiments were carried out in acetonitrile (MeCN). The molecule was dissolved in MeCN at low concentration (10^{-5} M) and titrated with a solution of sodium perchlorate (NaClO₄) or potassium perchlorate (KClO₄). Without alkali metal ions present, **PDI-crown** displayed the expected optical absorption band with three distinct peaks in the 450–550 nm range ascribed to the 0–0, 0–1, and 0–2 vibrational transitions.^[40] As shown in Figure 2b, upon titration with KClO₄ in MeCN, the absorption band changed including lowered intensity and peak broad-



Figure 2. a) Solution UV/Vis absorption spectra of PDI-crown and PDI-PEG at 10⁻⁵ M in chloroform; UV/Vis spectroscopy titration experiments of PDI-crown in acetonitrile (10⁻⁵ M) with b) KClO₄ and c) NaClO₄ (inset pictures show solutions at end point of titration); d) solution phase cyclic voltammetry of PDI-crown and PDI-PEG in dichloromethane (0.0005 M) with 0.1 M TBAPF₆ supporting electrolyte at 0.1 V · s⁻¹ scan rate; fluorescence spectroscopy titration experiments of PDI-crown in acetonitrile (10⁻⁵ M) with e) KClO₄ and f) NaClO₄; all experiments performed at room temperature.

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ening, accompanied by a change in the solution colour from yellow to pale pink, while no changes of the absorption profile were observed when NaClO₄ was added (Figure 2c). For the fluorescence spectra, the introduction of Na⁺ into a solution of PDI-crown in MeCN did not result in notable changes in emissive properties. However, the emission band with a maximum at 531 nm gradually decreased in intensity during the titration with K⁺. The same behaviours were found during the titration with sodium chloride (NaCl) or potassium chloride (KCl) in MeCN/H2O (8:2) mixture (Figure S14–S15). It is well known that fluorescence quenching could be induced by aggregation and strong intermolecular interactions.^[41-43] Our titration experiments indicate that K⁺ but not Na⁺ induces aggregation of **PDI-crown** units; this was seen not only from the emission quenching but also from the broadened absorption feature with K⁺ present, reflecting the presence of different non-aggregated and aggregated chromophores with different absorption profiles. As a control, we note that no significant spectral changes were observed when PDI-PEG was tested under identical conditions (Figure S16-S19) reinforcing the hypothesis that the crown ether drives the ion-selective responses. NMR titration experiments (Figure S12-S13) likewise supported the K⁺-driven aggregation manifested by significant signal broadening for both the aromatic and crown ether proton environments in the presence of KClO₄.

Further exploration of the cation-**PDI** complexes was employed in solid state arrangement. Thin spin-coated films of **PDI-crown** with 5 wt % polyethylene oxide were soaked in 0.1 M aqueous NaCl or KCl solutions, and UV/Vis absorption spectra were recorded at 5-minute intervals. As shown in Figure 3c, the main absorption feature of thin films soaking in KCl solution became broader after 5 minutes, while the absorption profile remained unchanged after soaking for 15 minutes in NaCl solution, indicating that K⁺ also causes a structural rearrangement when introduced into a densely packed **PDI-crown** thin film whereas Na⁺ again has a negligible effect.

To investigate redox activity and stability in an aqueous environment, solid-state cyclic voltammetry (CV) in aqueous NaCl and KCl electrolyte was tested (Figure S21–S24). Redox behaviours with an onset of reduction of -0.25 V versus Ag/Ag⁺ for **PDI-crown** and -0.23 V for **PDI-PEG** could be observed in KCl solution, and -0.25 V versus Ag/Ag⁺ for **PDI-crown** and -0.20 V for **PDI-PEG** in NaCl



Figure 3. Reductive thin film spectroelectrochemistry of PDIcrown: PEO blend films; thin films spin-coated onto ITO-coated glass substrates from 20 mg·mL⁻¹ chloroform solutions with 5 wt% PEO in a) 0.1 M KCl and b) 0.1 M NaCl supporting electrolyte; c) UV/Vis thin film absorption spectra of PDI-crown: PEO blends soaked in 0.1 M KCl and 0.1 M NaCl solutions.

solution. To improve thin-film adhesion and uniformity, high molecular weight polyethylene oxide (PEO, M_v 5000 kDa, 5 wt %) was blended with the **PDI**-based small molecules before thin-film deposition.^[44,45] The blends exhibited onsets of reduction similar to the neat thin films, and electrochemical cycling stability was slightly improved for both blends compared to the neat **PDI** films (Figure S21–S24).

Reductive thin film spectroelectrochemistry of PDIcrown blended with 5 wt % PEO was performed in aqueous electrolyte to investigate the electrochemical doping. For the PDI-crown: PEO film in NaCl electrolyte (Figure 3b), the neutral film shows the π - π * transitions at 482 nm, 500 nm and 550 nm. As the potential is gradually decreased to -0.4 V, the absorption band from the neutral state bleaches slightly. Simultaneously, a new absorption band ascribed to the radical anion appears with relatively narrow absorption peaks at 732 nm, 814 nm, and 994 nm. When the potential was returned to 0 V, the film returned to neutral state again, confirming the reversibility of the process. A different behaviour was observed in KCl electrolyte (Figure 3a); during the reduction, new broad peaks appear around 743 nm and 1090 nm, indicating the formation of the **PDI-crown** radical anion. Compared with the film in NaCl electrolyte, the new polaron absorption bands are much broader and of higher intensity when the same potential of -0.3 V was applied, while the bleaching of the neutral absorption band is also more pronounced, indicating that PDI-crown was more easily doped in KCl solution. However, the film did not return to its neutral state when the potential was reversed. Whereas the narrow polaron bands observed in the presence of Na⁺ are characteristic for the radical anion of an isolated PDI chromophore,[46-48] the much broader features observed with KCl electrolyte support the hypothesis of molecular aggregation taking place when K⁺ is present.

To gain deeper insights into the interactions between **PDI-crown** units in the presence of Na^+ and K^+ cations, we performed conformational analyses on PDI-crown:cation systems at the molecular mechanics and molecular dynamics levels, using the COMPASSIII force field (see Supporting Information for technical details). Our numerical simulations on PDI-crown: cation (1:2) systems reveal a snug fit of Na⁺ cations within the crown ether cavities, while the larger K^+ cations are observed to reside atop the crown ethers. Upon considering larger **PDI-crown**: cation (2:2) systems, we observe that K⁺ cations are sandwiched between two crown ethers, whereas Na⁺ cations exhibit strong interactions with one crown ether and modest interactions with half of the adjacent crown ether. To evaluate the propensity for **PDI-crown** aggregation in the presence of Na^+ and K^+ , we calculated complexation energies between a PDI-crown:caation (1:2) system and a second PDI-crown molecule (see SI). Our simulations indicate a stronger tendency for K⁺ systems to aggregate (Figure 4), with larger complexation energies stemming from the sandwiched arrangement of K⁺ ions between two crown ethers, consistent with spectroscopic data. Furthermore, our simulations suggest that the stability of **PDI-crown**:K⁺ assemblies will be significantly

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Figure 4. Conformational and energetic analysis of PDI-crown: cation assemblies. The reported values (in kcal/mol) correspond to the relative COMPASSIII-calculated complexation energies.

influenced by the ratio of **PDI-crown** to K^+ cations, as higher ion concentrations may disrupt the integrity of the sandwiched assemblies (Figure S26).

The mixed ionic and electronic transport characteristics of PDI-crown were investigated in an OECT setting. Devices were fabricated with channel dimensions of 100 µm by 10 µm (width/length). The active layer was spin-coated from 20 mg·mL⁻¹ chloroform solution containing also 5-20 wt % high molecular weight PEO to ensure thin film stability (see above). Both aqueous NaCl and KCl electrolytes (0.1 M) were used and dropped onto the channel, and an Ag/AgCl paste was used as the gate electrode. As shown in Figure 5a, the PDI-crown OECTs switched on upon application of positive gate voltages only in the KCl electrolyte, whereas no current modulation was observed in the NaCl solution. We note that no working OECTs were obtained with PDI-PEG as the active material. Testing 5, 10 and 20 wt % PEO formulations, PDI-crown with 5 wt % of PEO showed the best performance with slightly higher current response ($\sim 10 \,\mu$ A) than with 20 % PEO (Figure 5a).



Figure 5. Characterisation of PDI-crown based OECTs; all active layers spin-coated from 20 mg·mL⁻¹ PDI-crown solutions in chloroform with PEO (Mv 5000 kDa). a) Transfer characteristics of PDI-crown based OECTs with different mass fraction of PEO in 0.1 M KCl and NaCl electrolyte; b) transfer, e) output and d) operational stability characteristics of PDI-crown (with 5 wt% PEO) based OECTs in 0.02 M KCl electrolyte; c) transfer and f) output characteristics of PDI-crown (with 5 wt% PEO) based OECTs in 0.02 M NaCl electrolyte.

A relatively low operational stability was observed for this initial PDI-crown: PEO device in 0.1 M KCl electrolyte (Figure S27b). According to the computational modelling of the **PDI-crown**: cation systems (see above), the molecular aggregation becomes unstable if there are excessive cations. Hence, PDI-crown based OECTs were subsequently tested in lower concentrations of KCl and NaCl electrolytes (0.02 M). The **PDI-crown** based OECT operated with NaCl electrolyte does now show a small current response around $1 \mu A$; this is, however, starkly contrasted by the device operated in KCl with currents above 180 µA. Not only does the lower electrolyte concentration improve the current response of the **PDI-crown**:K⁺ system by more than an order of magnitude, it also allows us to quantify a difference between **PDI-crown**: Na^+ and **PDI-crown**: K^+ of more than two orders of magnitude in terms of OECT current response, clearly highlighting the ion-selective response. We also note that the operational stability of PDI-crown based devices in 0.02 M KCl electrolyte improved significantly in comparison to devices in 0.1 M KCl (Figure 5d); a similar trend is observed for the CV cycling stability comparing 0.02 M and 0.1 M electrolyte concentrations (Figure S21 and S23).

We ascribe the ion-selective OECT operation to the sandwich-like structure that is formed when K⁺ interacts with the 15-crown-5 motifs. This leads to extensive molecular aggregation with close π -stacking distances between neighbouring PDI units, as supported by our spectroscopic and computational analyses, and therefore the possibility for delocalised charge carriers and long-range electronic charge transport. With Na⁺, on the other hand, the preference for a 1:1 crown:cation stoichiometry is not conducive to structural reorganisation, most likely leading to localised charge carriers and thus much poorer device performance. The OECT devices, especially when operated in dilute electrolyte solutions, show significant counterclockwise hysteresis. We tentatively ascribe this to the strong interactions between the crown ethers and the cations, providing an energetic barrier to reverting to the neutral state as also observed during our spectroelectrochemical analysis. Further work is required to fully understand and take advantage of this behaviour.

In summary, we have designed and synthesised PDIcrown, a perylene diimide small-molecule semiconductor with pendant 15-crown-5 motifs with binding affinity to alkali metal ions such as Na⁺ and K⁺. While Na⁺ fits snugly inside the crown ether of **PDI-crown**, the larger K^+ sits outside the crown ether with the ability to bind to two crown motifs in a sandwich-like fashion. This behaviour is experimentally supported by signatures of molecular aggregation such as broadened absorption and quenched emission features for neutral **PDI-crown** with K⁺ but not with Na⁺ and in strong agreement with our computational results. Our spectroelectrochemistry studies likewise support the notion of delocalised charge carriers in the form of molecularly aggregated **PDI-crown** radical anions with K⁺ but not with Na⁺. Finally, we utilise this distinct difference in behaviour to create an ion-selective sensor using an OECT platform with PDI-crown as channel material; a

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range charge transport channels in the solid state.

Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords: aggregation · ion-sensing · mixed ionic-electronic conduction · n-type organic semiconductors · perylene diimide

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