Control of Crystallinity of Vinylene-Linked Two-Dimensional Conjugated Polymers by Rational Monomer Design

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Abstract: The interest in two-dimensional conjugated polymers (2D CPs) has increased significantly in recent years. In particular, vinylene-linked 2D CPs with fully in-plane sp²-carbon-conjugated structures, high thermal and chemical stability, have become the focus of attention. Although the Horner-Wadsworth-Emmons (HWE) reaction has been recently demonstrated in synthesizing vinylene-linked 2D CPs, it remains largely unexplored due to the challenge in synthesis. In this work, we reveal the control of crystallinity of 2D CPs during the solvothermal synthesis of 2D-poly(phenylene-quinoxaline-vinylene)s (2D-PPQVs) and 2D-poly(phenylene-vinylene)s through the HWE polycondensation. The employment of fluorinated phosphonates and rigid aldehyde building blocks is demonstrated as crucial factors in enhancing the crystallinity of the obtained 2D CPs. Density functional theory (DFT) calculations reveal the critical role of the fluorinated phosphate in enhancing the reversibility of the (semi)reversible C–C single bond formation.

Introduction

While linear (1D) conjugated polymers (CPs) have been extensively studied in the past decades due to their intrinsic semiconducting behavior,[1] the dimensional increase to two-dimensional (2D) CPs remained unexplored for decades. Since the discovery of graphene, with its semimetallic behavior, zero bandgap, and high charge carrier mobility,[2–6] the bottom-up synthesis of 2D CPs has become appealing for polymer and materials scientists. In particular, imine-linked (C–N) 2D covalent organic frameworks (2D COFs),[7–9] which can also be regarded as π-conjugated 2D CPs, have gained considerable interest in recent years. Nevertheless, the polarization of the carbon-nitrogen bond in the above-mentioned C=Н linkage cannot promote efficient conjugation through the 2D backbone.[10] For this reason, recent attention has been focused on carbon-conjugated 2D CPs due to their enhanced π-conjugation over the sp²-carbon frameworks and high stability compared to the imine-linked 2D COFs. Thus, 2016 marks the ascent of vinylene-linked 2D CPs by employing the Knoevenagel polycondensation.[10] The dimensional increase from linear conjugated polymers to 2D CPs is of particular interest due to the faster-evolving bandgaps[11] and enhanced chemical and physical properties, including chemical and thermal stabilities, and increased charge carrier transport compared to their linear counterparts.[12–16]

Due to the atomically precise integration of (functional) building blocks into ordered and porous sp²-carbon-conjugated structures with π-delocalization in two dimensions, vinylene-linked 2D CPs have been demonstrated as an efficient light emitter,[17,18] artificial photosystem (1[19] in catalysis,[20,21]...
formation of the \textit{trans}-vinylene \textit{VI}_{a}\textsuperscript{b} thus increasing the reversibility of the \textit{C--C} single bond formation; iii) Moreover, the fluorinated \textit{AB} model compound \textit{VI}_{a}\textsuperscript{b} (–185 kJ/mol) is more thermodynamically favored than the non-fluorinated \textit{VI}_{a}\textsuperscript{b} (–170 kJ/mol) model compound. The same trend can be also observed for electron-poor pyrazine and benzothiadiazole phosphonates for the HWE reaction (Supporting Information, Figure S11). To obtain insights into the reaction speed of the HWE reaction, time-dependent \textsuperscript{1}H NMR measurements were studied (Supporting Information, Figure S10). Applied \textsuperscript{1}H NMR studies of the reaction of phosphonate 1 or 2 with benzaldehyde (\textit{CsCO}_{2}H, mesitylene (\textit{Mes})/N,N-dimethylacetamide (DMAC) (1:1), 120°C) revealed a higher reaction speed for the deprotonation of the fluorinated phosphonate 2. Time-dependent NMR measurements after 5, 30, 60, 120, and 1200 min reaction time show an almost quantitative conversion/deprotonation of fluorinated phosphonate \textit{2} after 30 min, while phosphonate 1 remains incompletely converted after 20 h. Those findings are congruent to the above DFT calculations and reports in the literature.\textsuperscript{[36]} Nevertheless, despite the difference in reactivity, the isolated yields of 1,4-di((E)-styryl)benzene (3,
78 %) and ((1E,1'E)-(perfluoro-1,4-phenylene)bis(ethene-2,1-diyl))dibenzene (4, 76 %) are comparable for the respective model compounds (Figure 2b). Thereby, the improved understanding of the model reactions of phosphonates can be beneficial for the synthesis of novel 2D conjugated polymers with improved crystallinity using the semi-reversible HWE reaction.

Next, we compare the A₂B₂-type polycondensations of 1,3,5-tris(4-formyl-phenyl) benzene (TFPB, 5) or 2,4,6-tris(4-formyl-phenyl)-1,3,5-triazine (TFPT, 6) as aldehyde monomer together with 1 or 2 as phosphonate building blocks and Cs₂CO₃ as a base in a mixture of DMAc and o-DCB (1 : 3) at 120 °C (Figure 2a).

For the applied monomer combinations, PXRD data (Figure 3a) reveals the formation of the crystalline fluorinated polymer 2D-F-PPV2 (2 + 6, yield ca. 70%), In contrast, the other monomer combinations 1 + 5 (PPV1), 2 + 5 (F-PPV1), and 1 + 6 (PPV2) only resulted in amorphous polymers (Figure 3b). The amorphous polymers are classified as PPVs, whereas the crystalline polymers are classified as 2D-PPVs. These findings reveal that the employment of electron-poor phosphonate 2 and aldehyde monomers with increased rigidity and decreased conformational degrees of freedom can outweigh low reversibility of the bond formation: TFPT (6) shows a planar structure (0.0°) of the triazine core with its attached phenyl rings (Figure 2d), while the external phenyl rings (37.6°) in TFPB (5)
are rather twisted (Figure 2c). The layered crystalline structure of 2D-F-PPV2 was manifested by experimental and simulated PXRD patterns (Figure 3a). For 2D-F-PPV2, a reflex at 2θ = 28° can be assigned to the (100) plane. Density-Functional Tight-Binding (DFTB [39]) was used to optimize the monolayer structures of 2D-F-PPV2 using the Self-Consistent-Charge (SCC-DFTB) method, including Lennard-Jones dispersion. Carbon, nitrogen, oxygen, and hydrogen atoms are described using the mio-0-1 parameter set [38]. The optimized monolayer, AA (eclipsed), AB (staggered), and slipped-AA structures are generated for LUMO, and Fermi level of different stacking modes of parameters of 2D-F-PPV2 patterns.

Refinement of 2D-F-PPV2 can be found in the Supporting Information. Pawley refinement of 2D-F-PPV2 was conducted with Accelrys’s Materials Studio 7.0 software against the observed experimental patterns. 2D-F-PPV2 reveals AA (eclipsed) stacking with unit cell parameters of a = 37.4 Å, b = 37.4 Å, c = 3.5 Å, α = 90.0°, β = 90.0°, γ = 60° with agreement factors of Rwp = 3.68% and R1 = 2.58%.

The difference plot in Figure 3a reveals the consistency of the refined diffraction pattern with the experimental PXRD data. The FTIR spectra (Figure 3c) of PPV2 display characteristic absorptions around 3000–3300 cm⁻¹ (H valence vibrations, H)

Hatoms appearing at 950–1025 cm⁻¹ (v[P=O(EtO)2]). The 13C-NMR (Figure 3d) spectra of PPV1, F-PPV1, PPV2, and 2D-F-PPV2 show signals attributed to the vinylene C atoms appearing at ca. 130 and 140–144 ppm, respectively. The triazine C atoms of the TFPT moieties appear at shifts of 131 ppm (PPV1, 2D-F-PPV2), whereas the tertiary C atoms of the fluorinated moieties (from building block 2) appear at 114 ppm (F-PPV1, 2D-F-PPV2).

Motivated by the above results, we further investigated the role of the fluorinated phosphonate 2 on the crystallinity and expanded the investigation to other 2D CPs. Therefore, we synthesized the literature-reported 2D-PPQV1 [30] and the new 2D-F-PPQV1 in an A,B₂-type polycondensation by heating 2,3,8,9,14,15-hexa(4-formylphenyl)diquinoxalino[2,3-a:2',3'-a]phenazine (HATN-6CHO, 7), (fluorinated) phosphonate 1 or 2 and Cs2CO3 as a base in a mixture of Mes/DMAc (1:1) in a sealed glass ampule at 150 °C for three days (Figure 4a).

The crystalline layered structure of 2D-F-PPQV1 was revealed by experimental and simulated PXRDs (Figure 4c). 2D-F-PPQV1 reveals its first reflex at 2θ = 3.6°, which is attributed

![Figure 4](https://example.com/figure4.png)
to the (110) plane. Besides, a broad reflex at around 2θ = 5.5° to 8.1° appears, assignable to the (210) and (220) planes. The combined (210) and (220) reflex appears only for the fluorinated 2D-F-PPQV1. Based on the appearance of higher-order reflexes and the slightly lower full-width at half maximum (FWHM) of the first reflex (2D-PPQV1: ca. 1.4°, 2D-F-PPQV1: ca. 1.2°), we identify a superior crystallinity of 2D-F-PPQV1 (see the comparison in Supporting Information, Figure S1), which can be attributed to the combination of HATN-CHO (7) with its planar core (0.11°, Figure 4b) and the employment of electron-poor phosphate 2. Experimentally, the formation of crystalline 2D-F-PPQV1 is favored. For 2D-F-PPQV1, we observed larger cell parameters for the optimized monolayer, AA (eclipsed), AB (staggered), and slipped-AA structures, than those from the experimental PXRD; therefore, a fourth structural motif, where linkers connect obliquely to the next cell (that is, layer one connects to layer two), was optimized (AA mismatch). Optimized interlayer distances, relevant energies, bandgaps, unit cell parameters, HOMO, LUMO, and Fermi level of different stacking modes of 2D-F-PPQV1 can also be found in the Supporting Information. 2D-F-PPQV1 adopts AA layer mismatch stacking with unit cell parameters of a = 28.5 Å, b = 28.2 Å, c = 3.5 Å, α = 90.8°, β = 90.6°, γ = 57.1° with agreement factors of R SP = 0.84% and R p = 0.60%. The difference plot in Figure 4c shows the consistency of the refined pattern with the experimental PXRD data. Similar to 2D-F-PPV2, the FTIR spectrum (Figure 4d) of 2D-F-PPQV1 displays characteristic absorptions around 3000–3300 cm⁻¹ [aromatic C–H valence vibrations, v(C–H)], at 1595–1602 cm⁻¹ [vinylene stretches v(C=C)] as well as –CHO end groups [v(C=O), 1680–1703 cm⁻¹] and phosphate end groups [v(P=O–C), 950–1025 cm⁻¹]. Moreover, analogous to 2D-F-PPV2, the 13C-ssNMR (Figure 4e) spectrum of 2D-F-PPQV1 shows signals of vinylene C (130 ppm) atoms and secondary/tertiary benzene ring C atoms at chemical shifts at ca. 130 and 140–144 ppm, respectively. Furthermore, the 13C-ssNMR spectra of 2D-F-PPV2 and 2D-FPPQV1 reveal a low-intensity signal matching the presence of –CH₂PO(OEt)₂ end groups (ca. 15 and 35 ppm).

Nitrogen physisorption analysis at 77 K revealed the permanent porosity and pore size distribution of the layered crystalline 2D-F-PPV2 and 2D-F-PPQV1. The Brunauer-Emmett-Teller (BET) surface area was 290 and 186 m²/g, respectively (Supporting Information, Figure S3). In both cases, the isotherm shows a rise in the low-pressure range (P/P 0 = 0–0.05), typical for type-I nitrogen sorption. Trapped oligomers and structural defects might explain the moderate BET surface areas. Additionally, a type H4 low-pressure hysteresis can be found in both cases, which can be associated with the deformation of nonrigid pores’ walls. Density functional theory was used to determine the pore size distributions, revealing a pore size of approximately 18 Å to 29 Å (1.8–2.9 nm) for 2D-F-PPV2, which is smaller than the theoretical value (ca. 3 nm). 2D-F-PPQV1 shows a dual-pore distribution with approximately 1.0 Å and 1.9 Å (1.0–1.9 nm), matching well with the theoretical values (ca. 1.0 and 1.7 nm) and the reported values of 2D-PPQV1.[30] The layered morphology of the synthesized 2D CPs was revealed by high-resolution transmission electron microscopy (HR-TEM) and additionally scanning electron microscopy (SEM) characterizations (Supporting Information, Figure S12).

Next, the optoelectronic properties of the PPVs PPV1, F-PPV1, PPV2, and 2D-F-PPV2 were investigated by UV-Vis absorption and fluorescence spectroscopies (dispersion in 2-propanol). The UV-Vis spectrum (Figure 5a) shows the absorption edge at 463, 473, 490, and 485 nm, respectively. The measured absorption edges correspond to optical band gaps of 2.8, 2.8, 2.6, and 2.6 eV, respectively (Tauc plots in Supporting Information, Figure S5). The fluorescence spectrum (Figure 5b) exhibits an emission maximum at 485, 510, 507, and 538 nm for PPV1, F-PPV1, PPV2, and 2D-F-PPV2, respectively. Interestingly, the emissions of the fluorinated PPVs (F-PPV1 and 2D-F-PPV) show a bathochromic shift of up to 30 nm compared to their non-fluorinated counterparts (PPV1 and PPV2). The PPQVs 2D-F-PPQV1 and 2D-PPQV2 show absorption edges at 552 and 598 nm (ΔEg = 2.3 and 2.2 eV, Tauc plots in Supporting Information, Figure S4), respectively (Figure 5c), while the fluorescence spectra show maxima at 583 and 627 nm, respectively. Surprisingly, for the 2D-PPQVs, we do not observe an enlarged Stokes shift for the fluorinated 2D CP, possibly due to the lower influence of the fluorinated moieties on the overall optoelectronic properties.

Moreover, in contrast to the UV-Vis absorption in 2-propanol and 10 M NaOH, the absorption spectra of 2D-F-PPV2 in 10 M HCl demonstrated a bathochromic shift to absorption edges around 600 nm (Figure 5d and UV-Vis in Supporting Information, Figure S8). This shift can be explained by a lack of charge separation due to the resulting cationic resonance structures.[30] The chemical stability of 2D-F-PPV2 and 2D-F-PPQV1 was investigated by immersing them into sodium hydroxide solution (10 M NaOHaq) or hydrochloric acid (10 M HClaq) for

![Figure 5. a) UV-Vis absorption and b) fluorescence spectra (λex = 375 nm) of PPV1 (yellow), F-PPV1 (blue) PPV2 (red) and 2D-F-PPV2 (black) (dispersions in 2-propanol). c) UV-Vis absorption (solid lines) and fluorescence spectra (dashed lines, λex = 400 nm) of 2D-F-PPQV1 (black) and 2D-PPQV1 (red) (dispersions in 2-propanol). Photographs of d) 2D-F-PPV2 dispersions in 2-propanol, 10 M NaOH, and 10 M HCl.](image-url)
three days, respectively. PXRD and IR spectra of 2D-F-PPV2 and 2D-F-PPQV1 proved their unchanged crystallinity and chemical identity (Supporting Information, Figure S7). Moreover, thermogravimetric analysis (TGA) of 2D-F-PPV2 and 2D-F-PPQV1 reveals good thermal stability up to 400 °C (Supporting Information, Figure S9).

Conclusion

In summary, we demonstrated the crystallinity control of novel vinylene-linked 2D CPs using the HWE polycondensation by rational monomer design. Experimentally, we conclude that using rigid and planar building blocks compensates a poor reversibility and error correction. Besides, our experiments show that electron-poor fluorinated phosphonates can increase the crystallinity of the HWE reaction. Those findings are supported by DFT calculations indicating a higher energy barrier for the fluorinated phosphonates, possibly increasing the reversibility of the C–C single bond formation. The structures of the layered 2D CPs were elucidated by PXRD, nitrogen physisorption measurements, IR, 13C-ssNMR, etc, providing insights into the nature of the novel crystalline and porous 2D-F-PPV2 and 2D-F-PPQV1. Interestingly, the fluorescence spectra of the fluorinated PPVs (F-PPV1 and 2D-F-PPV) showed a bathochromic shift of up to 30 nm compared to their non-fluorinated counterparts (PPV1 and PPV2), while the fluorinated 2D-F-PPQV1 shows a hypsochromic shift of ca. 44 nm in comparison to non-fluorinated 2D-F-PPQV1. This work thus contributes to the in-depth understanding of the HWE polycondensation to enable the development of unprecedented vinylene-linked 2D CPs with enhanced crystallinity and novel functions.

Acknowledgements

This research was supported financially by the Graphene Flagship Core 3, the Collaborative Research Centre (CRC) 1415 “Chemistry of Synthetic Two-Dimensional Materials” (No. 417590517), H2020-MSCA-ITN (ULTIMATE, No. 813036), the ERC Consolidator Grant “T2DCP”, and the Coordination Networks: Building Blocks for Functional Systems (SPP 1928, COORNET). We thank M. Sc. Lukas Sporrer for SEM measurements, Dr. Kejun Liu for TEM measurements, M. Sc. Tobias Nickel for PXRD and NMR measurements, Dr. Valeriya Tkachova for mass spectrometry, Matthias Kluge for TGA measurements. We also acknowledge B. Sc. Max Klotzsche and M. Sc. Cindy Rau for practical support as a student research assistant. Furthermore, we recognize using the facilities in the Dresden Center for Nanoanalysis (DCN) at the Technische Universität Dresden. Computational resources were provided by the Center for Information Services and High-Performance Computing (ZIH) of the Technische Universität Dresden. Furthermore, MAA thanks the Materials Chemistry Consortium for HPC time on Young EP/T022213. Open Access funding enabled and organized by Projekt DEAL.

Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

Keywords: 2D covalent organic frameworks (2D COFs) · 2D conjugated polymers · Horner-Wadsworth-Emmons reaction · sp2 carbon-conjugated · vinylene- linked

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