Structural Chemistry (2025) 36:937–946
https://doi.org/10.1007/s11224-024-02423-0

RESEARCH

Construction of biphenylene dimers and surface-bound layers to explore donor-acceptor interactions

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Received: 29 October 2024 / Accepted: 14 November 2024 / Published online: 26 November 2024

Abstract

Molecular complexes based on donor-acceptor interactions that involve π-systems with antiaromatic character are rarely studied. Herein, we report the synthesis of biphenylene derivatives as potential electron donor components in π-complexes. Molecules with two connected biphenylene units are suitable to probe the formation of differently folded complexes in solution, while biphenylene derivatives with a pendant triethoxysilane group can be used to functionalize solid surfaces and probe interfacial donor-acceptor complex formation. Our results show clear indication of complex formation in solution; however, no observable interaction was found on the surface using UV-vis spectroscopy.

Keywords Antiaromaticity · Biphenylene · Donor-acceptor complex · Surface · Tetracyanoethylene · Tetracyanoquinodimethane

Introduction

Organic co-crystal engineering [1] is a vibrant area of research targeting the preparation of functional organic materials beyond the covalent synthesis of carbon-carbon and carbon-heteroatom bonds. Non-covalent interactions between relatively simple organic molecules with structural and electronic complementarity may provide unique structures and properties [2]. Among the possible non-covalent interactions that can drive the assembly of organic co-crystals, π-π interactions between electron donor and acceptor units are of primary interest. These interactions can be accompanied with different degrees of charge transfer between the components that can be harnessed in organic optoelectronic and semiconducting applications [3, 4]. Donor-acceptor molecular complexes could also form at the confined environment of molecular layers, which is a comparably less explored area of research [5–11]. The development of such 2D systems could be useful in thin film electronic devices and sensors.

For complex formation, electron-rich polycyclic aromatic compounds are mostly used as electron donors, while electron poor alkenes, quinoid structures, and cyano- and fluoroarenes are common electron acceptor partners [12]. Polycyclic conjugated molecules with antiaromatic character rarely appear in the construction of organic co-crystals. From the latter compound class, the biphenylene (BP) framework has been investigated in more detail [13–23]. We have recently shown in a combined experimental and computational study that BP, as an electron donor, forms a weak molecular complex with electron accepting TCNE that does not affect the (anti)aromatic character of BP [24]. In the present contribution, we report the structure of the BP/TCNQ complex and the synthesis of BP dimers and a silane-functionalized BP derivative to explore donor-acceptor interactions both in solution and at interfaces. Preliminary result on their interactions with TCNE and TCNQ electron acceptors is also presented.

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Experimental

General remarks

Commercial reagents, solvents, and catalysts (Sigma-Aldrich, Fluorochem, and VWR) of reagent grade were purchased and used without further purification. Solvents for extraction or column chromatography were of a technical quality. Organic solutions were concentrated by rotary evaporation at 40 °C. Thin-layer chromatography was carried out on "Merck silica gel 60 F254" type UV-active silica sheets. Column chromatography was performed using a Teledyne Isco CombiFlash Rf+ automated flash chromatographer with "RediSep Rf GOLD" silica gel column at 25(±1) °C. The cartridge was filled with Zeochem "ZEOprep 60 25−40 µm" silica gel. NMR spectra were acquired on a Varian 500 (^{1}H 500 MHz, ^{13}C 126 MHz) or a Varian 300 (^{1}H 300 MHz, ^{13}C 75 MHz) NMR spectrometer. The residual solvent peaks were used as the internal reference. Chemical shifts (δ) are reported in ppm. The following abbreviations are used to indicate the multiplicity in ^{1}H NMR spectra: s, singlet; d, doublet; t, triplet; and m, multiplet. ^{13}C NMR spectra were acquired in a broadband decoupled mode. All NMR spectra were recorded at 30 °C. UV−vis absorption spectroscopy was executed on a Jasco V-750 spectrophotometer. High-resolution mass spectrometry measurements were performed on a Sciex TripleTOF 5600+ high-resolution tandem mass spectrometer equipped with a DuoSpray ion source. APCI ionization was applied in positive ion detection mode. Samples were dissolved in acetonitrile and flow injected into the acetonitrile/water 1:1 flow. The flow rate was 0.2 mL/min. The resolution of the mass spectrometer was 35,000.

Cannizzaro reaction of formylbiphenylene 3 to access compounds 1 and 2

2-Formylbiphenylene (**3**) [25] (500 mg, 2.77 mmol) was dissolved in MeOH (10 mL) and a solution of NaOH (5.55 g, 139 mmol) in distilled water (15 mL) was added. The reaction was heated at 80 °C for 18 h. After cooling the mixture to rt, water (85 mL) was added, and the aqueous mixture was extracted with CH_2Cl_2 (3×40 mL). The combined organic layer was dried ($MgSO_4$) and the solvent was evaporated under reduced pressure. The crude product was purified by column chromatography (SiO_2, hexane → hexane/EtOAc (40%)) to obtain alcohol **2** as a pale yellow solid (215 mg, 43%). ^{1}H NMR (500 MHz, $CDCl_3$) δ = 6.77–6.58 (m, 7H), 4.44 (s, 2H), 1.89 (s, 1H) ppm. ^{13}C NMR (126MHz, $CDCl_3$) δ = 151.89, 151.02, 150.87, 150.79, 141.20, 128.52, 128.41, 126.64, 117.63, 117.52, 117.15, 116.83 ppm.

The aqueous phase was acidified with HCl and extracted with EtOAc (3×40 mL). The combined organic layer was washed with water and brine, dried ($MgSO_4$), and concentrated under reduced pressure. The product carboxylic acid **1** was obtained as a yellow solid (220 mg, 41%). The product did not require further purification steps. ^{1}H NMR (500 MHz, acetone-d6) δ = 11.03 (bs, 1H), 7.61 (dd, J = 7.2, 1.1 Hz, 1H), 7.24 (s, 1H), 6.92–6.80 (m, 5H) ppm. ^{13}C NMR (126 MHz, Acetone-d6) δ = 167.11, 157.12, 152.29, 151.23, 150.72, 133.08, 131.35, 130.58, 129.89, 119.59, 119.20, 117.98, 117.72 ppm.

Synthesis of compound 4

A mixture of biphenylene-2-carboxylic acid (**1**) (100 mg, 0.51 mmol), K_2CO_3 (211 mg, 1.53 mmol), and CH_3I (401 µL, 6.44 mmol) in acetone (10 mL) was stirred at 60 °C for 16 h. The resulting mixture was filtered through a pad of celite, and the filtrate was concentrated in reduced pressure. The crude product was purified by column chromatography (SiO_2, hexane/EtOAc 9:1). The product (**4**) was obtained as a yellow solid (74.5 mg, 70%). ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.58 (dd, J = 7.3, 1.3 Hz, 1H), 7.21 (s, 1H), 6.85–6.66 (m, 5H), 3.86 (s, 3H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ = 166.80, 156.53, 151.48, 150.57, 149.99, 132.26, 130.04, 129.69, 128.93, 118.74, 118.32, 117.21, 116.80, 52.13 ppm.

Synthesis of compound 5

A mixture of biphenylen-2-ylmethanol (**2**) (50 mg, 0.27 mmol) and 4-dimethylaminopyridine (DMAP) (3.4 mg, 27.4 µmol) under inert atmosphere (N_2) was cooled to 0 °C in an ice bath. Subsequently, acetic anhydride (Ac_2O) (32 µL, 0.33 mmol) and *N*,*N*-diisopropylethylamine (DIPEA) (58 µL, 0.33 mmol) were added, and the reaction was stirred at 0 °C for 15 min. The resulting mixture was diluted with CH_2Cl_2 (50 mL) and washed with 1% HCl solution (3×15 mL). The organic phase was dried ($MgSO_4$), concentrated under reduced pressure, and the crude product was purified by column chromatography (SiO_2, hexane → hexane/EtOAc (10%)). The product (**5**) was obtained as a yellow solid (60 mg, >95%). ^{1}H NMR (300 MHz, $CDCl_3$) δ = 6.80–6.70 (m, 3H), 6.70–6.57 (m, 4H), 4.88 (s, 2H), 2.10 (s, 3H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ = 171.16, 152.08, 151.62, 150.96, 150.90, 136.19, 128.79, 128.77, 128.69, 117.93, 117.90, 117.85, 117.28, 66.95, 21.30 ppm.

General procedure for the synthesis of BP dimers 9–11

Biphenylen-2-ylmethanol (**2**) (1 equiv.), the dicarboxylic acid (0.5 equiv.), *N*,*N*′-dicyclohexylcarbodiimide (DCC) (1.1 equiv), and DMAP (0.025 equiv), under an inert atmosphere

(N_2), were cooled to 0 °C in an ice bath. Subsequently, acetonitrile (10 mL) was added, the ice bath was removed, and the reaction was stirred at rt for 1 h. The mixture was diluted with CH_2Cl_2, celite was added, and the solvent was evaporated under reduced pressure. The crude product was purified by column chromatography (dry-loaded on celite, SiO_2, hexane → hexane/EtOAc (25%)). The BP dimers were obtained as yellow solids.

*BP-dimer **9*** (253 mg, 80%). ^{1}H NMR (500 MHz, $CDCl_3$) δ = 6.78–6.73 (m, 4H), 6.71 (d, *J* = 7.0 Hz, 2H), 6.67–6.60 (m, 6H), 6.58 (d, *J* = 7.0 Hz, 2H), 4.94 (s, 4H), 3.46 (s, 2H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ = 166.38, 151.97, 151.69, 150.75, 150.70, 135.26, 128.74, 128.70, 128.67, 117.87, 117.82, 117.68, 117.14, 67.81, 41.77 ppm. HRMS (APCI) *m/z*: $[M]^{\cdot+}$ calcd for $C_{29}H_{20}O_4$ 432.1361; found, 432.1341.

*BP dimer **10*** (152 mg, 62%). ^{1}H NMR (500 MHz, $CDCl_3$) δ = 6.78–6.73 (m, 4H), 6.71 (d, *J* = 7.0 Hz, 2H), 6.67–6.60 (m, 6H), 6.58 (d, *J* = 7.0 Hz, 2H), 4.89 (s, 4H), 2.69 (s, 4H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ = 172.16, 151.92, 151.50, 150.80, 150.74, 135.85, 128.64 (2C), 128.54, 117.82, 117.76, 117.67, 117.14, 67.08, 29.36 ppm. HRMS (APCI) *m/z*: $[M]^{\cdot+}$ calcd for $C_{30}H_{22}O_4$ 446.1518; found, 446.1496.

*BP dimer **11*** (159 mg, 63%). ^{1}H NMR (500 MHz, $CDCl_3$) δ = 6.78–6.73 (m, 4H), 6.71 (d, *J* = 7.0 Hz, 2H), 6.67–6.61 (m, 6H), 6.59 (d, *J* = 7.0 Hz, 2H), 4.88 (s, 4H), 2.42 (t, *J* = 7.4 Hz, 4H), 1.99 (p, *J* = 7.4 Hz, 2H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ = 172.84, 151.93, 151.47, 150.81, 150.75, 136.02, 128.64 (2C), 128.52, 117.82, 117.76, 117.68, 117.15, 66.79, 33.43, 20.25 ppm. HRMS (APCI) *m/z*: $[M]^{\cdot+}$ calcd for $C_{31}H_{24}O_4$ 460.1674; found, 460.1653.

Synthesis of compound 12

Methyltriphenylphosphonium iodide (239 mg, 610 µmol) was dissolved in abs. THF (5 mL), cooled to 0 °C in an ice bath, and *n*-butyllithium (244 µL, 2.5 M, 610 µmol) were added dropwise and stirred for 30 min under N_2 atmosphere. Biphenylene-2-carbaldehyde (**3**) (100 mg, 555 µmol) was dissolved in abs. THF (5 mL) was transferred dropwise to the reaction mixture. The resulted suspension was stirred at rt for 1 h. After completion of the reaction, the product mixture was diluted with CH_2Cl_2 (30 mL), and the resulting solution was washed with water (50 mL) and brine (20 mL). The organic phase was dried ($MgSO_4$) and the solvent was removed by rotary evaporation. The crude product was purified by flash column chromatography (SiO_2, *n*-hexane) to obtain 2-vinylbiphenylene **12** as a yellow solid (52.6 mg, 53%). ^{1}H NMR (500 MHz, $CDCl_3$) δ = 6.84 (s, 1H), 6.79 – 6.75 (m, 2H), 6.72–6.63 (m, 3H), 6.60 (dd, *J* = 7.1, 0.6 Hz, 1H), 6.53 (dd, *J* = 17.5, 10.9 Hz, 1H), 5.61 (d, *J* = 17.5 Hz, 1H), 5.15 (d, *J* = 10.9 Hz, 1H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ = 151.68, 151.02, 150.90, 150.72, 138.02, 137.21, 128.63, 128.50, 127.96, 117.72, 117.59, 117.40, 114.09, 112.76 ppm.

Synthesis of compound 13

2-Vinylbiphenylene **12** (128 mg, 718 µmol) was dissolved in triethoxysilane (1 mL) in a vial and purged with argon. Pt/C (14 mg, 2 mol%) was added and the mixture was stirred at 120 °C for 24 h. Subsequently, the reaction mixture was diluted with EtOAc (10 mL) and filtered through a pad of celite, which was washed with small portions of EtOAc several times. The solvent was removed by rotary evaporation and the crude product was purified by flash column chromatography (SiO_2, *n*-hexane) to obtain compound **13** as a yellow oil (61 mg, 25%, contains small amount of triethoxysilane as impurity). ^{1}H NMR (500 MHz, CD_2Cl_2) δ = 6.75–6.69 (m, 2H), 6.66–6.50 (m, 5H), 3.81 (q, *J* = 7.0 Hz, 6H), 2.55–2.46 (m, 2H), 1.22 (t, *J* = 7.0 Hz, 9H), 0.91–0.84 (m, 2H) ppm. ^{13}C NMR (75 MHz, CD_2Cl_2) δ = 151.86, 151.60, 128.75, 128.39, 127.11, 118.50, 117.75, 117.66, 117.41, 58.90, 30.02, 18.71, 12.82 ppm (not all quaternary carbons are observable due to low intensity).

X-ray crystallographic analysis

Single crystals of BP/TCNQ could be obtained from DCM solution by slow evaporation. A suitable crystal was selected and mounted on a loop on a Rigaku R-Axis Rapid II Spider diffractometer. The crystal was kept at 294.15 K during data collection. Using Olex2 [26], the structure was solved with the olex2.solve [27] structure solution program using Charge Flipping and refined with the olex2.refine [27] refinement package using Gauss-Newton minimization. Crystal data and structure refinement parameters are shown in Table S1 (Supporting Information). CCDC deposition number 2384673 contains further supplementary crystallographic data for this paper.

Single crystals of **10** could be obtained from THF solution by slow evaporation. A suitable crystal was selected and mounted on a loop on a XtaLAB Synergy-R, HyPix diffractometer. The crystal was kept at 113.7(3) K during data collection. Using Olex2 [26], the structure was solved with the SHELXT [28] structure solution program using Intrinsic Phasing and refined with the SHELXL [28] refinement package using Least Squares minimisation. Crystal data is shown in Table S1 (Supporting Information). CCDC deposition number 2384674 contains further supplementary crystallographic data for this paper.

Quartz surface modification with compound 13

Compound **13** (12 mg, 35 µmol) was dissolved in a mixture of THF (12 mL) and cyclohexane (50 mL). Subsequently, 70 µL hydrochloric acid (di. water/cc. HCl 8:1) was added to the mixture and stirred for 30 s. Quartz slides (previously washed with piranha solution, di. water and dried under a N_2 flow) were immersed in 10 mL portions of the reagent solution at rt for different times. After surface modification, the slides were washed with acetonitrile (spectroscopic grade) and dried under a N_2 flow, and the solid-phase UV-Vis spectrum of each slide was recorded.

Results and discussion

We have recently shown that biphenylene (BP), as an electron donor, forms a weak molecular complex with electron accepting TCNE [24]. In the crystal structure of the complex, the two components were found non-co-planar with only a moderate overlap between the π-systems. Furthermore, the molecular planes were not parallel but tilted by an angle of 9.84° with respect to each other (Fig. 1a). As a comparison, we crystallized the BP/TCNQ complex (Fig. 1b) from CH_2Cl_2 solution (BP/TCNQ 1:1) that formed mixed stacks of alternating donor and acceptor molecules in a 1:1 ratio, similarly to the BP/TCNE complex. However, in contrast to the BP/TCNE system, a large intrastack molecular overlap between the π-systems of the donor BP and the acceptor TCNQ was observed with an interplane distance of 3.287 Å.

To test the effect of multiple donor units on the formation and stability of these complexes, we explored the synthesis of BP dimers and their interactions with acceptor molecules TCNE and TCNQ. We envisioned the formation of complexes with possibly different arrangements depending on the interacting donor and acceptor components (Fig. 2a, b). Furthermore, as a complementary strategy, we aimed at the synthesis of a BP derivative that is suitable for covalently bound layer formation on solid surfaces (Fig. 2c).

For the synthesis of BP dimers, we considered two approaches using the relatively straightforward esterification chemistry of BPs: **A** based on the reaction of biphenylene-2-carboxylic acid (**1**) with diols and **B** based on the reaction of 2-biphenylenemethanol (**2**) with dicarboxylic acids (Fig. 3).

The crucial difference between the two structures is the position of the electron withdrawing carboxyl group relative to the BP unit. In design **A**, where it is directly attached, the electron donor BP is somewhat more electron deficient

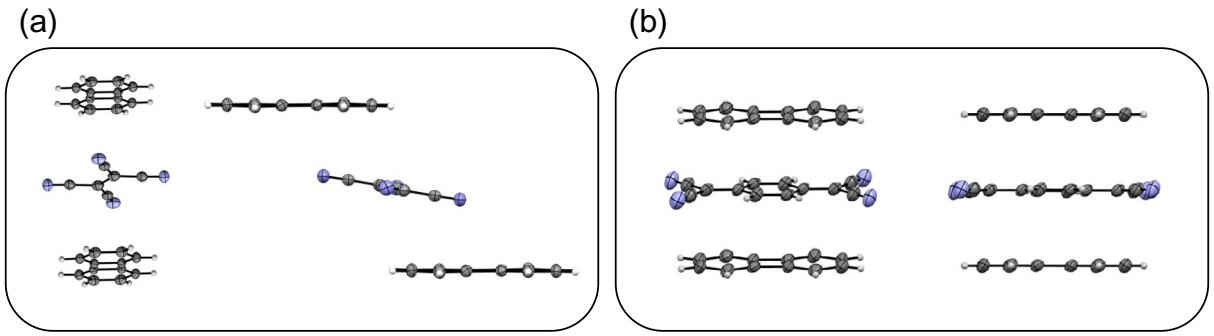

Fig. 1 X-ray crystal structure of the BP/TCNE complex (**a**) and the BP/TCNQ complex (**b**) (ORTEP style representation is drawn at the 50% probability level)

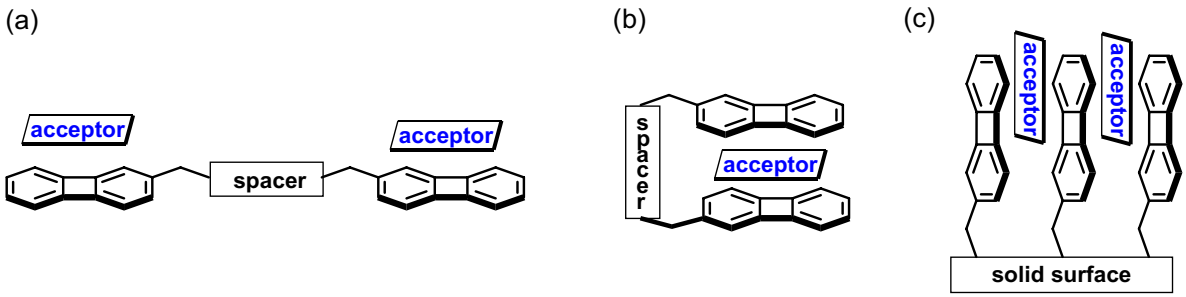

Fig. 2 Potential interactions between BP dimers (**a**, **b**) and surface bound BP layers (**c**) with electron acceptors

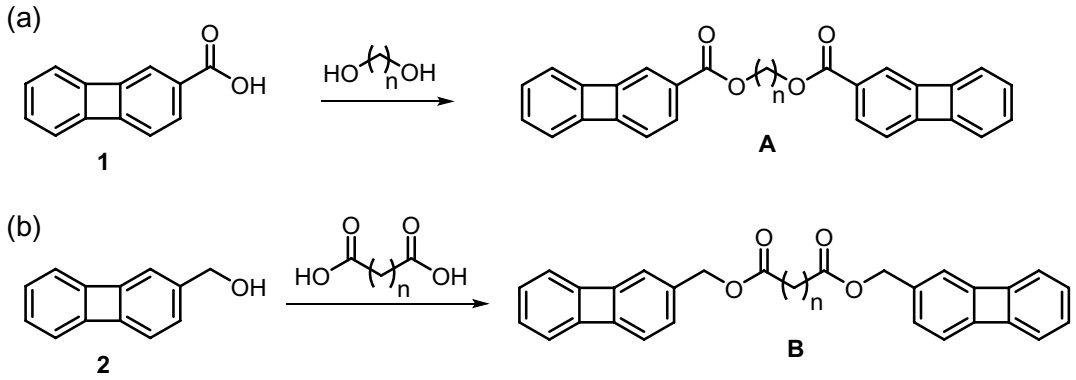

Fig. 3 Different esterification strategies to construct molecules with two BP units

compared to the second, **B**, where the electron withdrawing group is decoupled from the BP ring system by a methylene group.

To probe the effect of these arrangements, we synthesized two control molecules **4** and **5** (Fig. 4). To access these compounds, instead of synthesizing the carboxylic acid (**1**) and the alcohol (**2**) separately, we explored the disproportionation of the relatively easily accessible aldehyde **3** through the Cannizzaro reaction (Fig. 4a) [29]. It turned out to be an efficient approach that required only NaOH as reagent, while providing both **1** and **2** in a single step in good yields. Subsequently, acid **1** was converted to its methyl ester **4** using MeI for the *O*-alkylation reaction (Fig. 4b), and the alcohol **2** was reacted with acetic anhydride to give the benzyl acetate type product **5** in high yield (Fig. 4c).

We looked at the changes in the optical properties of esters **4** and **5** upon mixing them with TCNE and TCNQ in CH_2Cl_2 (10^{-2} M solutions were used to prepare the mixtures due to the absence of apparent complex formation in more diluted solutions) (Fig. 5). The colour changes of the yellow solutions of the BP derivatives were immediately apparent in contact with the acceptor compounds. The appearance of a blue colour in all cases indicated the formation of molecular complexes, which was also supported by UV-vis measurements. In the UV-vis spectra of the **4**/TCNE and **5**/TCNE systems, new bands appeared above 500 nm (λ_{max}(**4**/TCNE) = 624 nm, λ_{max}(**5**/TCNE) = 678 nm), where none of the individual components showed absorptions (Table 1). The new absorption bands were the most intense at 1:1 component ratio, although variations in the ratios (1:1, 1:2, 2:1) showed little effect on the intensity of the new absorption bands. This suggests that the formation of the 1:1 complex dominated in solution. Notably, in the case of the **5**/TCNE mixture, the new absorption band was more intense compared to that observed for the **4**/TCNE mixture. This finding can be paralleled with the electronic considerations in the molecular design. In compound **4**, the electron withdrawing ester group is directly connected to BP that decreases its electron donating character. On the other hand, in compound **5**, the ester moiety is connected to the BP unit through a

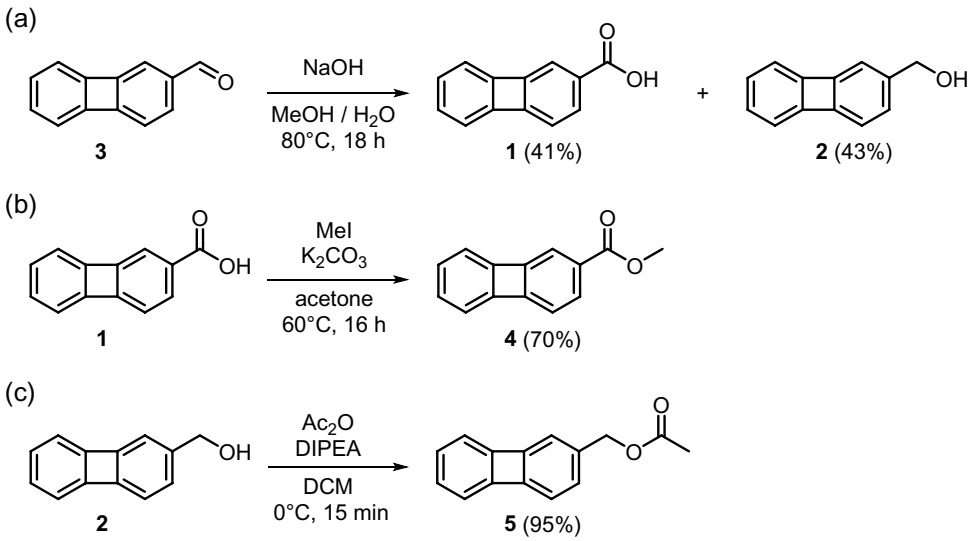

Fig. 4 Synthesis of BP esters. **a** Cannizzaro reaction of BP aldehyde **3**; **b** *O*-alkylation of biphenylene-2-carboxylic acid **1** with MeI; **c** *O*-acylation of biphenylen-2-ylmethanol **2** with Ac_2O

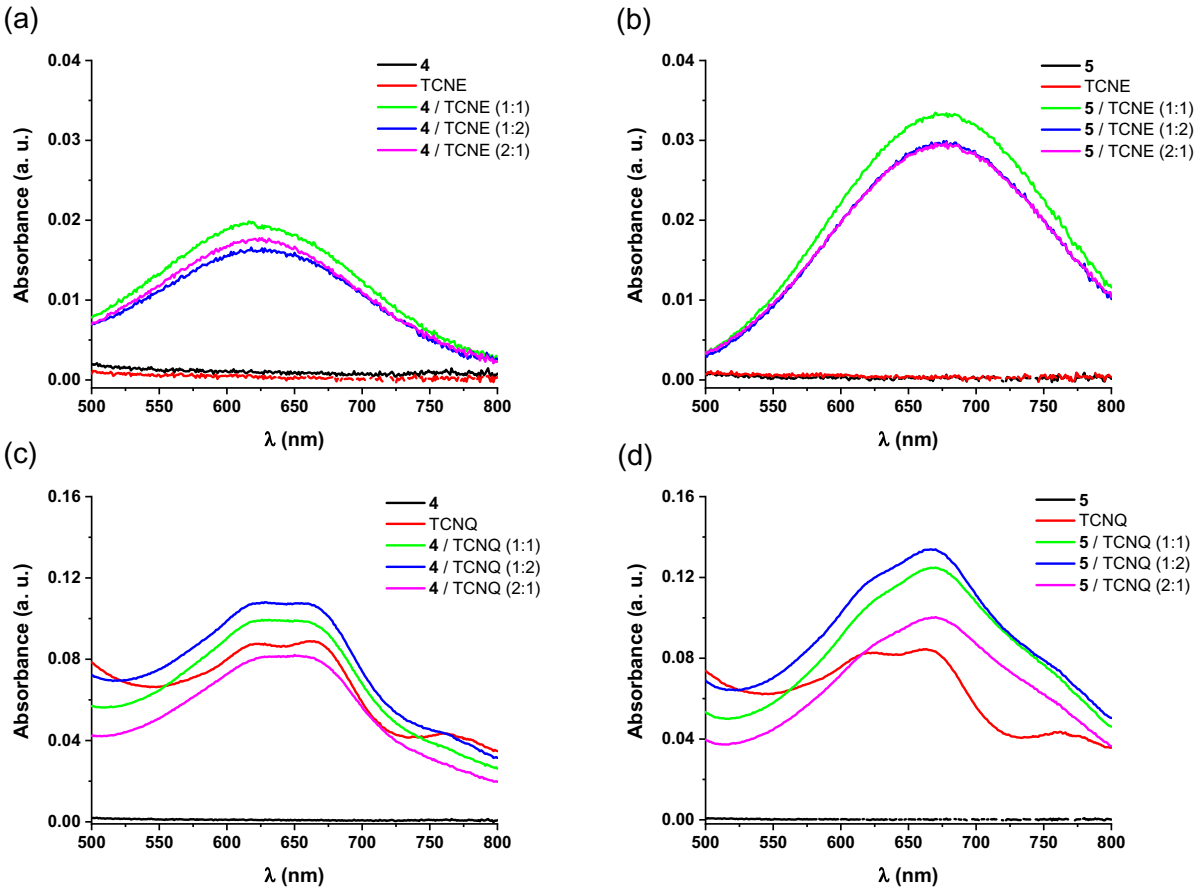

Fig. 5 The charge transfer bands in the UV-vis spectra upon interaction of BP esters **4** and **5** with TCNE (**a**, **b**) and TCNQ (**c**, **d**) in CH_2Cl_2 at rt

Table 1 Position of the charge transfer bands in the UV-vis spectra of the different complexes of compounds **4** and **5**

D/A ratio	λ_{max} (nm)			
	4/TCNE	5/TCNE	4/TCNQ	5/TCNQ
1:1	624	678	620–660	670
1:2	624	678	620–660	670
2:1	624	678	620–660	670

methylene group that eliminates the direct electron withdrawing effect. These variations in the donating ability of the BP units are likely responsible for the changes in intensity and λ_{max} values in the UV-spectra of the mixtures.

The observations for the **4**/TCNQ and the **5**/TCNQ systems were qualitatively similar to those containing TCNE; however, some of their features were somewhat different. These solutions were prepared identical to the TCNE containing systems. The formation of complexes with TCNQ was evident by the colour changes; however, the new absorption bands overlapped with the spectrum of pristine TCNQ that contains bands in the same spectral region (550–700 nm). The effect of the TCNQ ratio was stronger on the absorption intensity compared to that of TCNE. Both **4**/TCNQ and **5**/TCNQ absorptions showed maximum intensity at 1:2 ratio followed by the 1:1 and 2:1 mixture. The excess amount of uncomplexed TCNQ could contribute to differences in intensity due to spectral overlap. Analogously to the TCNE containing systems, the stronger interaction between compound **5** with TCNQ compared to that of **4** likely accounts for the stronger absorption intensity and shifted λ_{max} values in the UV-spectrum in this case.

Generally, the overall stronger interaction of the BP derivatives with TCNQ than with TCNE is reflected in the appearance of higher intensity absorptions for **4**/TCNQ and **5**/TCNQ compared to the **4**/TCNE and **5**/TCNE.

Based on these results, we experimentally considered BP dimers of type **B**, where the ester moieties are electronically decoupled from the donor BP units with a methylene group.

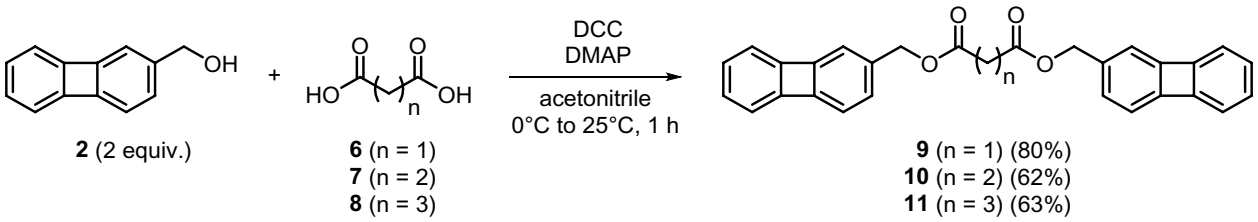

Fig. 6 The general synthetic route applied to access esters **9**–**11**

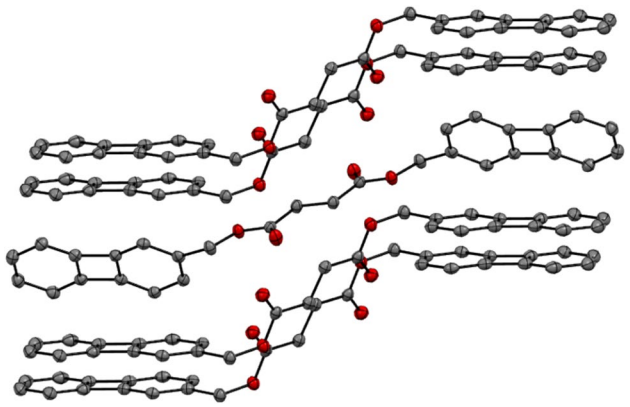

Fig. 7 X-ray crystal structure of compound **10** (ORTEP style representation is drawn at the 50% probability level; H atoms are omitted for clarity)

We synthesized three structures using different dicarboxylic acids leading to different carbon chain lengths between the ester groups (Fig. 6). The coupling of alcohol **2** and reagent dicarboxylic acids **6**–**8** using DCC as the coupling agent provided the dimers **9**–**11** in good yields.

Compound **10** could be crystallized for single crystal X-ray diffraction measurements (Fig. 7). In the solid state, the dominant part of the inter- and intramolecular interactions involved the oxygen atoms of the ester groups.

Compounds **9**–**11** exhibited similar UV-vis absorption profiles, independent of the number of carbon atoms between the ester units (Fig. 8a). None of them showed absorption bands in the visible region. Upon addition of TCNE and TCNQ to BP dimers **9**–**11**, the observed spectral changes (Fig. 8b–d and Table 2) were similar to that of **5**/TCNE and **5**/TCNQ, respectively. The intensities of the new bands were largely independent of the component ratio at this concentration range (10^{-2} M solutions in CH_2Cl_2 were used to prepare the mixtures). Unfortunately, no single crystals of the molecular complexes could be obtained.

As a complementary strategy, we synthesized a BP derivative with a triethoxysilane group for surface attachment (Fig. 9). We used aldehyde **3** to access vinylbiphenylene **12** via a Wittig olefination with methyltriphenylphosphonium iodide. In a subsequent Pt-catalyzed hydrosilylation reaction with triethoxysilane, compound **13** could be isolated. We expected that this molecule will be suitable for the covalent modification of Si-based solid surfaces.

We treated quartz slides with a slightly acidic solution of compound **13** in THF/cyclohexane [30] and followed the changes in their absorption profile over time using UV-vis spectroscopy (Fig. 10a). The absorptions that are characteristic of BP (Fig. 10b) appeared even after 1 h and became more intense up to 24 h treatment. This suggests that the silanization of the surface with compound **13** was successful.

However, upon immersion of the surfaces into CH_2Cl_2 solutions of TCNE and TCNQ with different concentrations (5×10^{-5}, 4×10^{-3}) for different times (1, 3, 8, 24, and 48 h), no charge transfer complex formation was observable by UV-vis spectroscopy. This could be due to the small number of molecules involved in persistent donor-acceptor interactions on the surface, which is below the detection limit by UV-vis spectroscopy, while crowding effects could also play a role [31]. Nevertheless, this surface bound BP system might be suitable for the study of interfacial π-molecular complexes with other analytical techniques in the future.

Conclusion

We prepared new BP derivatives that are suitable to study the formation of molecular π-complexes in different environments. The synthesis of molecules that contain two BP chromophores was realized using the Cannizzaro reaction to access the necessary BP precursors. These compounds with two pendant BP electron donors provide the opportunity to study the formation of different supramolecular assemblies guided by donor-acceptor interactions. We also synthesized a BP derivative that is suitable for surface attachment

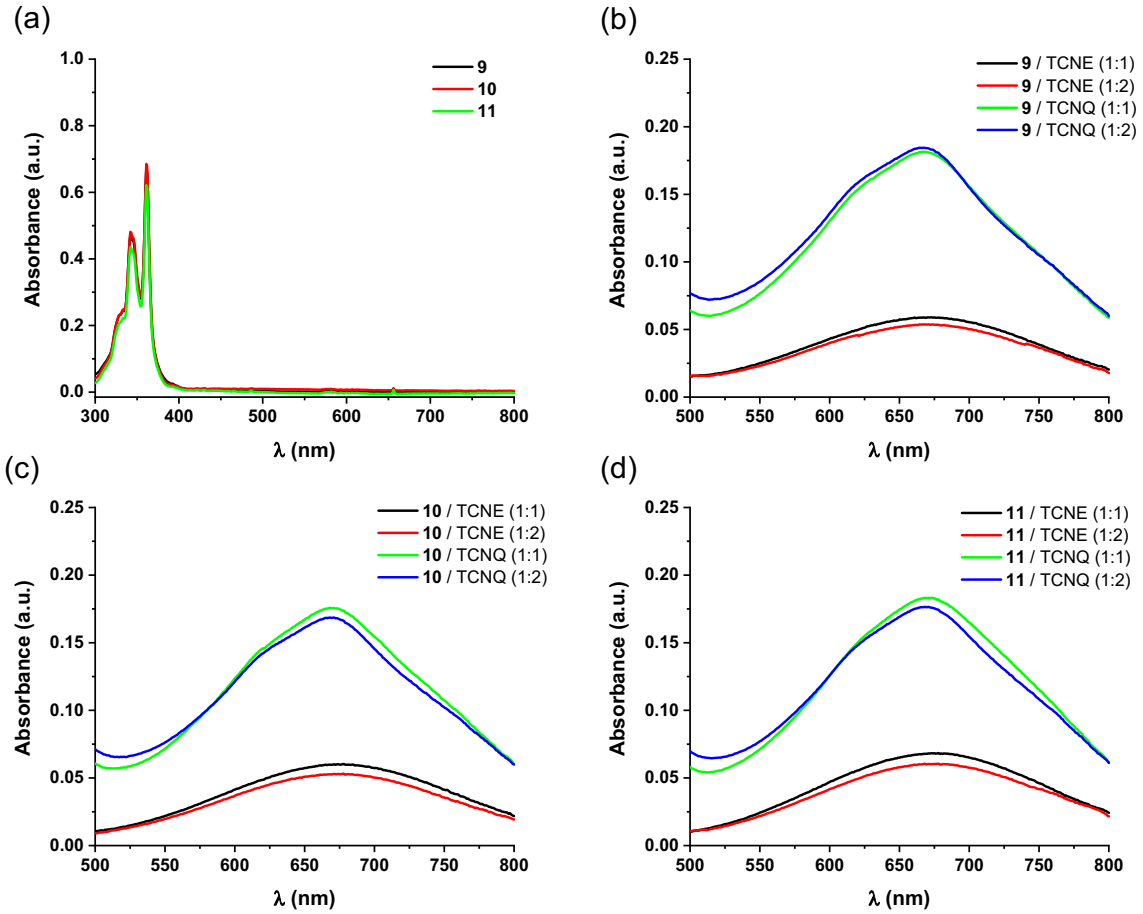

Fig. 8 **a** The UV-vis spectra of compounds **9**–**11**; **b**–**d** the charge transfer bands in the UV-vis spectra upon interaction of BP esters **9**, **10**, and **11** with TCNE and TCNQ in CH_2Cl_2 at rt

Table 2 Position of the charge transfer bands in the UV-vis spectra of the different complexes of compounds **9**–**11**

D/A ratio	λ_{max} (nm)					
	9/TCNE	10/TCNE	11/TCNE	9/TCNQ	10/TCNQ	11/TCNQ
1:1	673	678	678	668	668	673
1:2	674	678	678	667	668	668

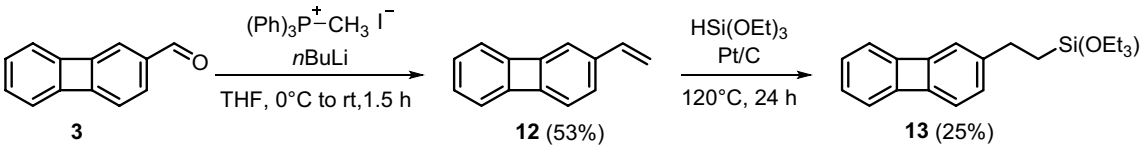

Fig. 9 Synthesis of the triethoxysilane containing BP (**13**)

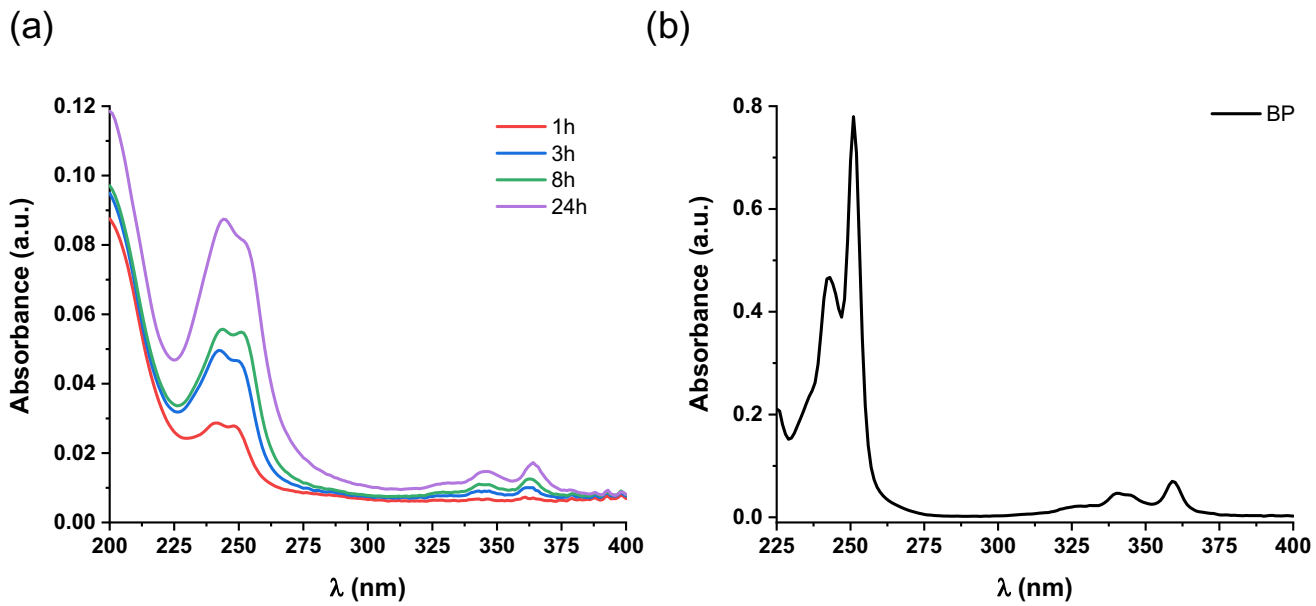

Fig. 10 **a** Solid-state UV-vis spectra of quartz slides immersed in the solution of **13** for different times; **b** UV-vis spectrum of BP in CH_2Cl_2 at rt

through its triethoxysilane function. Surface assemblies could be useful to probe complex formation in confined environments and could be the basis for sensing acceptor type analytes. We used TCNE and TCNQ acceptors to probe the interaction of the electron donor and acceptor partners. Our preliminary results show that both TCNE and TCNQ form complexes with the dimeric BP chromophores; however, so far, we did not succeed in growing suitable single crystals for the structural analysis of the complexes. Measurements involving the surface attached BP donor and the TCNE and TCNQ acceptors did not show apparent complex formation using UV-vis spectroscopic detection.

Supplementary Information The online version contains supplementary material available at https://doi.org/10.1007/s11224-024-02423-0.

Author contribution K. Molnár., R. Dobszay, P. T. Szabó, T. Holzbauer and A. Kunfi, performed the experimental work. All authors contributed to the data analysis. A. Kunfi and G. London wrote the original draft. All authors have read and agreed to the published version of the manuscript.

Funding Open access funding provided by HUN-REN Research Centre for Natural Sciences. Financial support from the Hungarian Academy of Sciences through the Lendület Program (LENDULET_2018_355) (G.L.) and the National Research, Development and Innovation Office, Hungary (NKFIH Grants No. PD 137866 (A.K.), FK 142622 (G.L.) is acknowledged. G.L. acknowledges the János Bolyai Research Scholarship from the Hungarian Academy of Sciences. The crystallographic study was carried out using the infrastructure of Eötvös Loránd University Institute of Chemistry (ELTE-CrystalLab) and HUN-REN-ELTE Protein Modelling Research Group and it was supported by the European Union and the State of Hungary and co-financed by the European Regional Development Fund (VEKOP-2.3.3-15-2017-00018).

Data availability Data is provided within the manuscript or supplementary information files.

Declarations

Conflict of interest The authors declare no competing interests.

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