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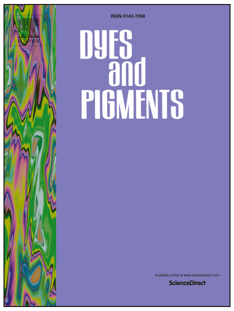

Novel functionalized indigo derivatives for organic electronics

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Novel functionalized indigo derivatives for organic electronics

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ABSTRACT

A series of nine novel indigo derivatives, including diiodoindigo, octahalogenated indigoids and compounds with extended *π*-conjugated system, were synthesized, characterized and investigated as semiconductor materials in organic field-effect transistors (OFETs). Among them, 6,6'-diiodoindigo demonstrated the ambipolar behavior with balanced *p*-type and *n*-type mobilities. The complete substitution of hydrogens at the indigo core with halogen atoms led to low electron mobilities in OFETs. An extension of the conjugated system through the introduction of small aromatic substituents (thiophene and phenyl) resulted in predominant *p*-type behavior. Fusion of aromatic rings resulted in *z*-shaped dibenzoindigo, which showed poor charge transport properties due to the non-optimal arrangement of molecules along each other in the crystal lattice. The acquired data fulfilled the previously reported model based on the relationship between the chemical nature of substituents and their positions at the indigo core, optoelectronic properties of materials and their performance in OFETs. The results of this study will be useful for rational design of a new generation of the indigo-based semiconductors for biocompatible organic electronics.

Keywords: indigo, indigoids, organic field effect transistors, semiconductors, OFET

INTRODUCTION

There is a constantly increasing demand for various electronic devices. However, their components based on inorganic compounds are at reasonable risk to once confront the limited availability of key elements (such as Li, In, and Ga), in addition to environmental issues related to their production and utilization.[1] In contrast, organic materials consist of widely distributed elements, many of their precursors can be obtained from biomass, and their preparation and purification are less energy-consuming. The continuous search for new organic semiconductor materials has already led to ongoing improvements of their performance in solar panels, light-emitting diodes, transistors, *etc.*[2],[3] Current efforts are aimed at improving stability and safety of developed materials and developing technologies for growth of high-quality semiconductor films.[4],[5],[6],[7],[8] Searches for new materials with desired properties have also covered the well-known natural dyes and pigments.[9],[10],[11] For instance, indigo and its derivatives are widely used in cosmetics, textile, food, printing inks, *etc.* as the colorants with low acute toxicity.[12],[13] Thus, some novel applications of these derivatives have been explored, *viz.*, as photoinitiators for the polymerization,[14] electrochemical doping of nanoporous anodic aluminum oxide,[15] in photodiodes,[16] as electroactive materials for Na-ion[17] and flow[18] batteries, as sensor materials for ozone[19],[18] and fluorine ions[20]. Indigo and its functionalized derivatives possess optimal optoelectronic and physicochemical properties to be applied as semiconductor materials in organic field effect transistors. Semiconducting properties of the parent compound (indigo) have been discovered in 2010s,[21],[22],[23] giving rise to chemical functionalization of indigo molecule as the method for design of novel materials with improved charge transport characteristics. Several works reported the application of 6,6'-dibromoindigo, 6,6'-dichloroindigo as semiconductors for OFETs.[24] Complementary-like inverters [25] and organic photodetectors [26] have been also designed and investigated. Our group has previously explored indigoids bearing halogen, cyano and trifluoromethyl

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an significantly affect HOMO and LUMO energy levels as well as the crystal structure of indigoids. Those observations could be helpful in the design of new indigoids with superior charge-transport properties and ambient stability.

Extension of *π*-conjugated system is an efficient approach to increase the charge carrier mobilities. As compared to pristine indigo, dibenzoindigo with two fused benzene rings demonstrates superior *p*-type transport properties. [28] Both 5,5'-diphenyl and 6,6'-dithienyl substituted indigoids exhibit well-balanced ambipolar behavior in OFETs.[29][30] However, the fabrication of devices using these compounds involves energy-consuming vacuum evaporation processing techniques, while inexpensive printing technologies require the solution-processible materials. Unfortunately, only a limited set of indigo-based soluble small molecules is currently known. Bisalkoxy-substituted derivatives have been synthesized, but demonstrated poor characteristics in OFETs.[31] Although bisalkyloxyphenyl indigo derivatives are capable of forming liquid crystalline phase, the charge carrier mobility has been never measured for these compounds.[32]

Thus, a very limited number of indigo derivatives was explored as potential components for the organic electronics, while the testing conditions were not unified, which does not allow making any clear comparison of the characteristics of transistors based on different compounds. No reliable relationships between their structure and performance in transistors have been established yet due to the lack of systematic research.

Herein we report on the design, synthesis, and investigation of a diverse set of indigo-based molecules (Figure 1) as promising materials for organic electronic devices. Common approach to their design is based on the introduction of electron-withdrawing groups in the case of *n*-type materials and on the expansion of conjugated electronic system for the *p*-type materials. Therefore, we have started from the introduction of halogen atoms, up to the complete substitution at benzene rings of the indigo core, followed by the evaluation of their performance as semiconductors in transistors. Novel derivatives incorporating aromatic substituents and fused structure **9** were also designed as the *p*-type materials.

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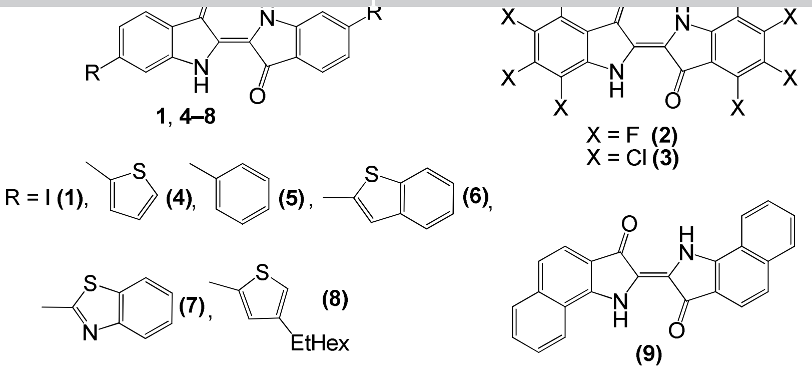
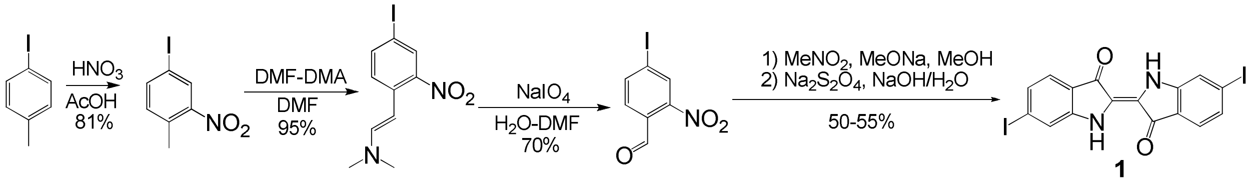


Figure 1. Chemical structures of the designed and investigated indigo derivatives.

RESULTS AND DISCUSSION

Molecular design and synthesis. Although the effect of iodine substituents at the indigo core on the material performance in OFETs has been already demonstrated for 5,5'-diiodoindigo,[33] our previous work has revealed that 6,6'-dihalogen isomers of indigoids possess superior semiconductor characteristics as compared to their 5,5'-analogues. [27] Thus, the number of considered indigo derivatives was extended with the corresponding *6,6'*-diiodoindigo.

Synthetic route towards 6,6'-diiodoindigo is shown on Scheme 1. Commercially available 4-iodotoluene was nitrated in glacial acetic acid to give 2-nitrotoluene. Then it was treated with *N,N*'-dimethylformamide dimethyl acetal and subsequently oxidized by $NaIO_4$, resulting in 4-iodo-2-nitrobenzaldehyde. Target 6,6'-diiodoindigo **1** was synthesized in the yield of 54% *via* Harley–Mason reaction consisting of two steps: (1) 2-nitrobenzaldehyde was treated with nitromethane in the presence of sodium methylate (Henry reaction) and (2) consequently reduced with sodium dithionite.



Scheme 1. Synthesis of 6,6'-diiodoindigo **1**.

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he decreased LUMO energy level, [27] so the full substitution of hydrogens by halogen atoms should shift energy levels even further. Different synthetic routes were used for the synthesis of indigo derivatives **2** and **3** bearing 8 halogen atoms (Scheme 2). The limiting step in the synthesis of octafluoroindigo was the alkylation of corresponding antranilic acid with bromoacetic acid (30% yield even after the optimization of reaction conditions). Intramolecular Claisen condensation of obtained carboxyaryl glycine led to diacetylindoxyle that was hydrolyzed with alkali to give indigo derivative **2**.

Similar alkylation did not occur in the case of tetrachloroantranilic acid due probably to the mesomeric effect of chlorine atoms. Target compound **3** was obtained *via* the treatment of tetrachloroantranilic acid with formalin. The subsequent ring opening of obtained formalide by potassium cyanide (CAUTION: highly toxic substance) led to 2,3,4,5-tetrachloro-6-((cyanomethyl)amino)benzoic acid. Alkali hydrolysis of nitrile and consequent intramolecular Claisen condensation resulted in tetrachloroindoxyl, the precursor of octachloroindigo **3**.

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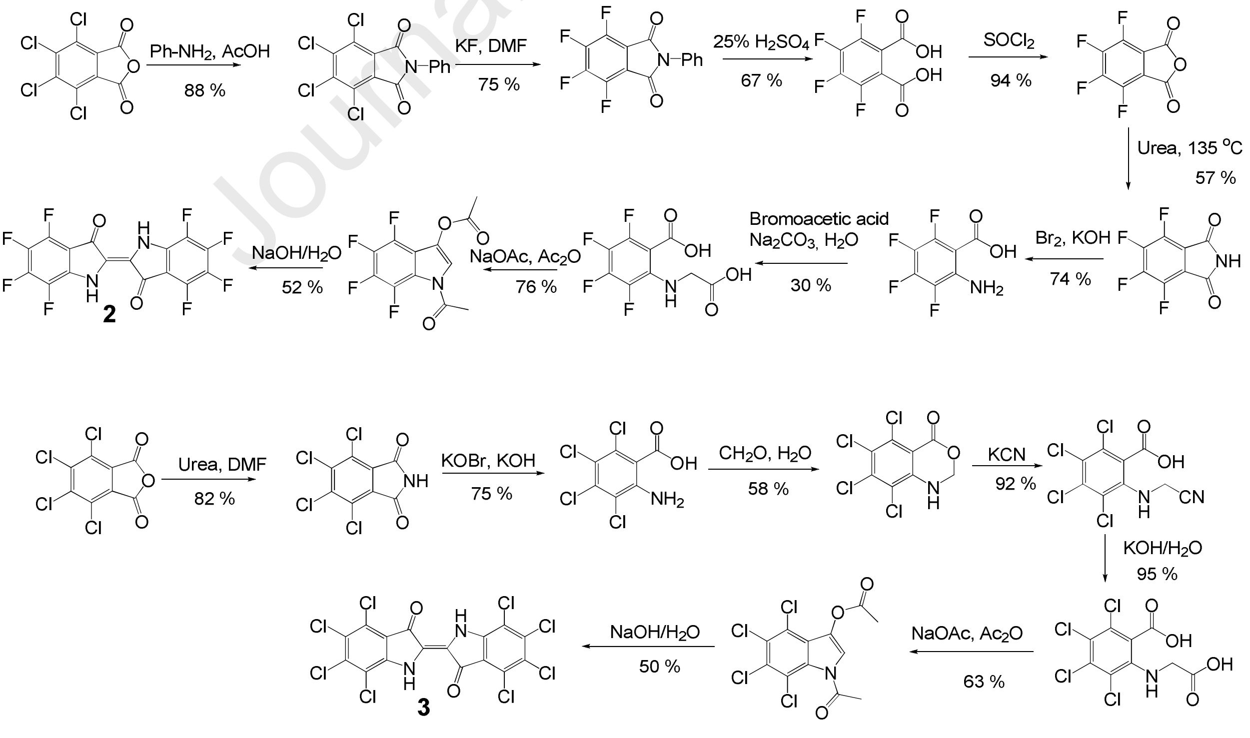
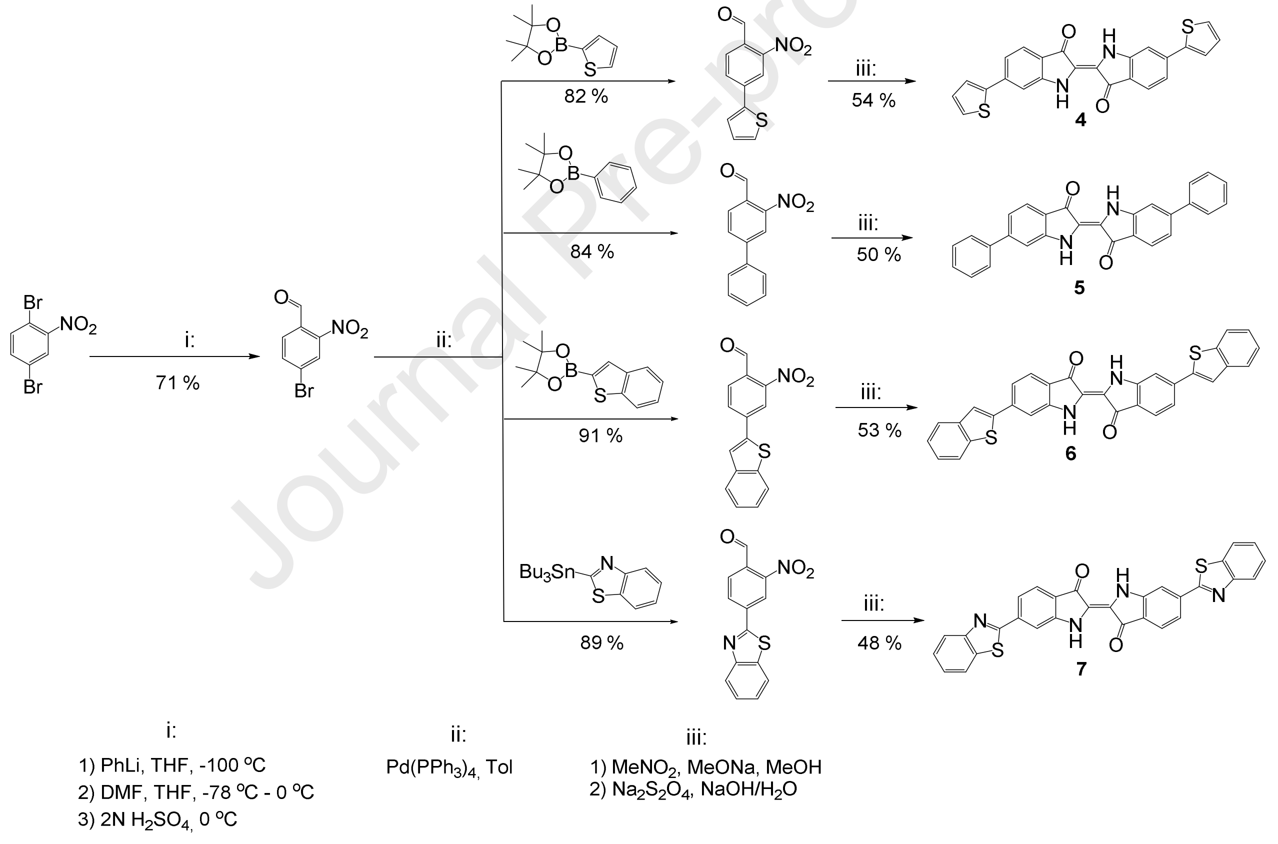


Scheme 2. Synthesis of indigo derivatives **2** and **3**.

gh-performance and air-stable ambipolar semiconductors,[30] so we have explored the possibility of substituting indigo at the 6,6' positions with phenyl, thienyl, benzothienyl and benzothiazolyl groups.

Synthetic routes towards indigo derivatives bearing phenyl, thienyl, benzothienyl and benzothiazolyl substituents are shown in Scheme 3. Commercially available dibromonitrobenzene was lithiated with phenyl lithium at -110 °C, followed by treatment with dimethylformamide resulting in 4-bromo-2-nitrobenzaldehyde. The Suzuki and Stille cross-coupling reactions with corresponding boronic acids and their ethers or with stannanes led to *o*-nitrobenzaldehydes that were converted into target compounds **4**-**7**.



Scheme 3. Synthesis of indigo derivatives **4**–**7**.

Soluble indigo derivative **8** comprising thiophene rings was obtained *via* the reaction of 6,6'-dibromoindigo with tributyl(5-(2-ethylhexyl)thien-2-yl)stannane according to Scheme 4.

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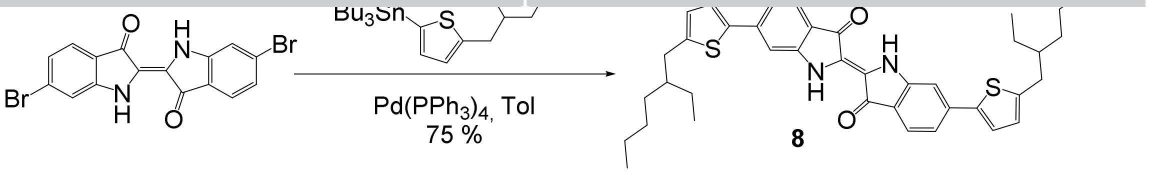
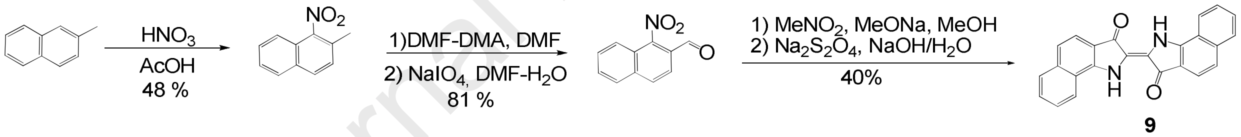


8

Scheme 4. Synthesis of soluble indigo derivative **8**.

Extension of π-conjugated system of indigo in novel fused derivatives is the efficient approach to design new semiconductor materials with enhanced properties. [28],[34],[35] Thus, another isomer of dibenzoindigo with the fused structure was designed. Synthesis of dibenzo[g,g']indigo is shown in Scheme 5. 2-Methylnaphtalene was nitrated with fuming nitric acid in glacial acetic acid to give 2-methyl-1-nitronaphtalene. It was subsequently oxidized with dimethylformamide dimethyl acetal and $NaIO_4$ to give 1-nitronaphthyl carbaldehyde. Its treatment with nitromethane and sodium methylate followed by the reduction with sodium dithionite led to target dibenzo[g,g']indigo **9**.



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Scheme 5. Synthesis of dibenzo[g,g’]indigo **9**.

All the obtained indigo derivatives (except for **8**) exhibited an extremely low solubility in organic solvents, making their NMR characterization quite challenging. However, all these compounds were characterized with mass spectroscopy, FTIR spectroscopy, and elemental analysis (ESI), while structures of some of them were completely confirmed by the single crystal X-ray diffraction analysis.

S**ingle crystal X-ray diffraction analysis** was carried out for compounds **1**, **8** and **9** (CCDC: 2013267, 2010617 and 2013266; See Table S1 for crystal data, data collection and structure refinement details). In all crystals studied molecules participate in the stacking interactions but the plane-to-plane distance as well as type of molecules overlap are different. (Fig. 2) The shortest

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ng value for **1** is 3.398□. As compared to parent indigo (intermolecular spacing of 3.40 Å), diiodoindigo **1** and dibenzoindigo **9** demonstrate the same or shorter π-π distances, thus suggesting the possibility for formation of efficient intermolecular contacts. In the case of alkylthienyl indigo **8**, its branched 2-ethylhexyl chains hinder close intermolecular contacts.

In addition to the different character of overlap of π-systems in stacks, a significant difference is observed for the mutual disposition of the π-stacked columns. Each molecule of **8** participates in the formation of four intermolecular N-H…O hydrogen bonds (N…O is 3.07Å) with two neighbouring molecules (Figure S1). These hydrogen bonds assemble molecules in slightly corrugated H-bonded layers and stacking-bonded columns, which are parallel to each other. In the diiodoindigo (**1**), each molecule also forms four N-H…O bonds (N….O 2.903 □) but with four neighbouring molecules in perpendicular dimensions (Figure S2). Such type of H-bonding assembles molecules into the three-dimensional framework and stacked-bonded columns are almost perpendicular (81°). Therefore, isotropic charge transport properties can be expected for diiodoindigo featuring it as a promising organic semiconductor material. The molecules of **9** do not participate in any intermolecular H-bonds that is rare for indigo derivatives and the angles between the stacking-bonded columns is equal to 62.6°. Despite of the differences in the H-bonding in **1**, **8** and **9** the strengths of the intramolecular N-H….O bonds in this derivatives are identical. Thus, one can conclude that the N…O distance for intramolecular interaction is solely governed by the conjugation.

It should be noted that the molecules are shifted along each other in the stacks, whereas the angle between the straight line connecting centers and planes of the molecules (see Figure S3 for definition of angle) is not 90° (expected for perfect H-type molecular stack), but is equal to 126, 147 and 154° for **1**, **8**, and **9**, respectively. It is known that shifting of the molecules with respect to each other reduces the charge transport mobility along the π-stack. [36], [37]

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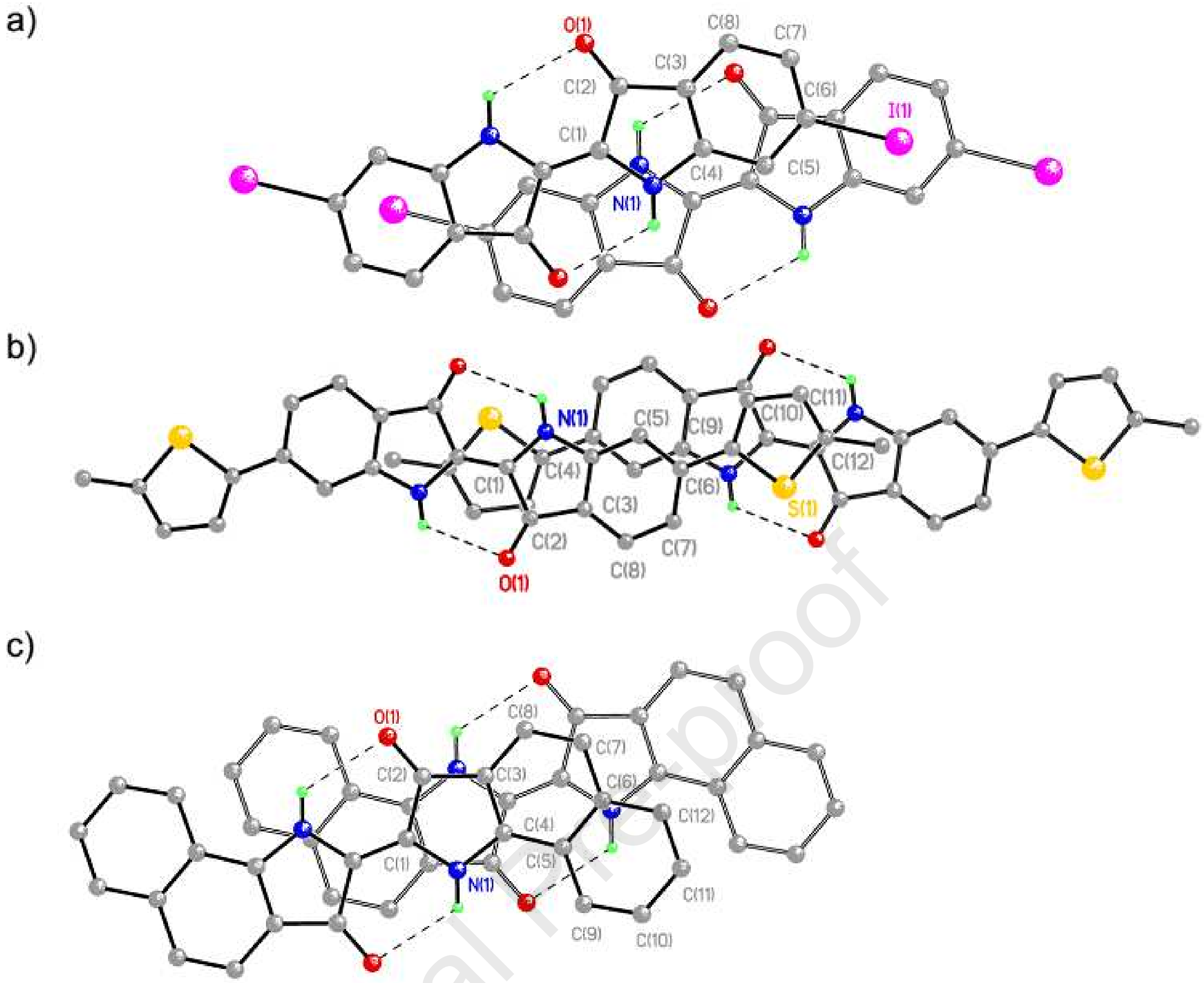

Figure 2. The molecules overlap in the stacked-bonded columns in **1** (a), **8** (b), and **9** (c). The alkyl substituents in 8 are omitted for clarity.

Optoelectronic properties of the obtained compounds. Figure 3a,b shows the absorption spectra of indigo derivatives dissolved in a hot 1,2-dichlorobenzene, wherein compounds **1–9** exhibit peaks, very similar to those of indigo in long-wavelength range. Compounds **3–8** afforded very small red shift as compared to indigo (600nm).

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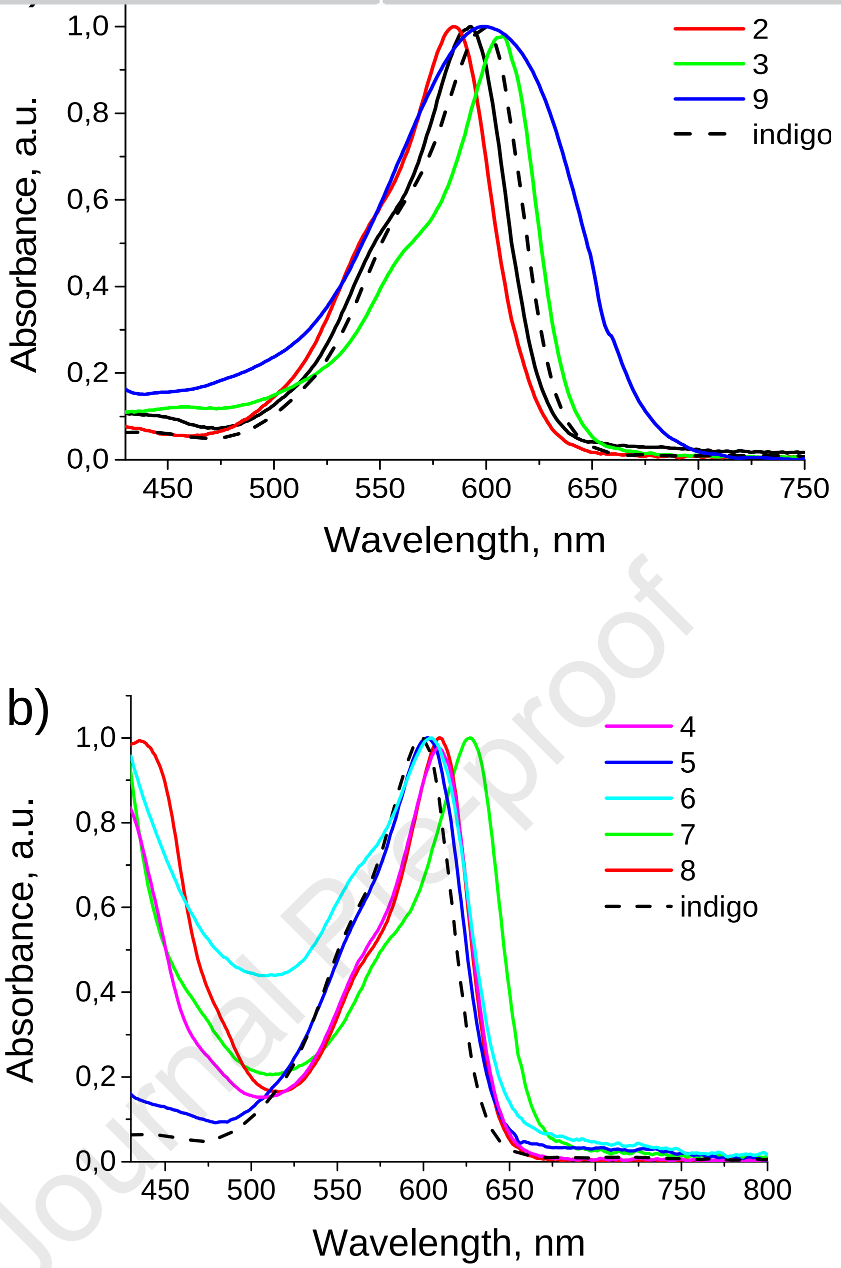

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Figure 3. Normalized UV-Vis spectra of indigo and its derivatives **1-9** in hot 1,2-dichlorobenzene.

Optical and electrochemical properties of indigo derivatives were also investigated in thin films, except for compound **6** due to its insufficient thermal stability and low solubility preventing film deposition by either of the vapor phase and solution techniques. All the other compounds demonstrated quite different optical spectra recorded for their solutions in hot 1,2-dichlorobenzene and thin films (ESI, Figures S4–S10). The spectra of compounds **2–6, 8,** and **9** in thin films are red-shifted with respect to those of the solutions. This suggests the formation of J-aggregates [38] in thin films, that does not facilitate the charge-transport properties. On the contrary, the spectra of

H-aggregates promoting the efficient charge transport.

Cyclic voltammetry measurements were performed for thin films deposited by the thermal evaporation on glassy carbon disc electrodes in order to reveal onsets of the oxidation and reduction waves for these compounds (ESI, Figure S11). Assuming that the Fermi energy for the Fc^+/Fc redox couple is - 5.1 eV, the HOMO and LUMO energies of the compounds were estimated according to the standard approach.[39] Table 1 summarizes the acquired data. Almost all the indigoids demonstrated close values of their reduction potentials, defining LUMO energies of ca. –3.9 eV. The introduction of fluorine or chlorine atoms has significantly decreased the LUMO levels below -4.0 eV, which is favoring ambient stability of the anion species. The HOMO energy levels were less affected by the substitution in indigo core.

It is known that indigo is a fairly stable pigment, which does not decompose up to 380 °C. [40] Most of the studied indigo derivatives also demonstrated comparably good thermal stability showing no weight loss below 400 °C as revealed by thermal gravimetry (ESI, Figure S12). An exception is compound **8** containing alkyl solubilizing chains, which substantially decrease the thermal stability of the material and it starts to decompose at the temperature as low as 200 °C.

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Compound	$\lambda_{max}^{Solution}$ (nm)	λ_{max}^{Film} (nm)	E_g^{Film} (eV)	E^{ox}_{ons} *vs.* Fc/Fc$^+$ (V)	HOMO (eV)	E^{red}_{ons} *vs.* Fc/Fc$^+$ (V)	LUMO (eV)
1	307, 359, 593	311, 375, 539	1.77	0.72	-5.82	-1.45	-3.88
2	304, 584	330, 645	1.76	0.75	-5.85	-0.91	-4.19
3	311, 607	311, 621	1.80			-1.02	-4.08
4	334, 417, 609	327, 410, 560, 635	1.73	0.67	-5.77	-1.15	-3.95
5	311, 373, 602	315, 378, 620	1.66	0.69	-5.79	-1.16	-3.94
6	334, 394, 628	n/a*	n/a	n/a	n/a	n/a	n/a
7	340, 606	348, 566	1.72	0.59	-5.69	-1.16	-3.94
8	332, 436, 610	330, 415, 628	1.71	0.8	-5.90	-1.18	-3.92
9	303, 374, 398, 600	322, 380, 400, 533, 664	1.72	0.73	-5.83	-1.20	-3.90
I	300, 600	335, 665	1.71	0.67	-5.77	-1.20	-3.90

* It was impossible to obtain thin films of compound **6** due to its decomposition during evaporation.

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Electrical properties of materials in field effect transistors. The synthesized indigo derivatives were investigated as semiconductor materials in OFET devices with the architecture shown in Figure 4a. It is known that dielectric material can affect the ordering of semiconductor molecules in thin films [41], whereas using additional passivation coatings can eliminate the surface trap states, improve charge carrier mobility and reduce hysteresis. [42],[43] Therefore, bare alumina AlO_x and its combinations with cross-linked benzocyclobutene derivative (BCB) or normal-chain hydrocarbon tetracontane ($C_{40}H_{82}$, TC) passivation coatings were used as dielectrics to investigate the electron and hole transport properties of the materials (See ESI for detailed procedure of the behavior in OFETs. Table 2 shows major characteristics of the assembled devices.

Diiodoindigo **1** demonstrated ambipolar behavior with balanced mobility in both channels in the case of TC used as the dielectric (Table 2, Figure 4b). Octafluoroindigo **2** and octachloroindigo **3** did not exhibit semiconductor properties in combination with all the three selected dielectrics, while only very low electron mobility was detected for octafluoroindigo **2** in combination with plain AlO_x.

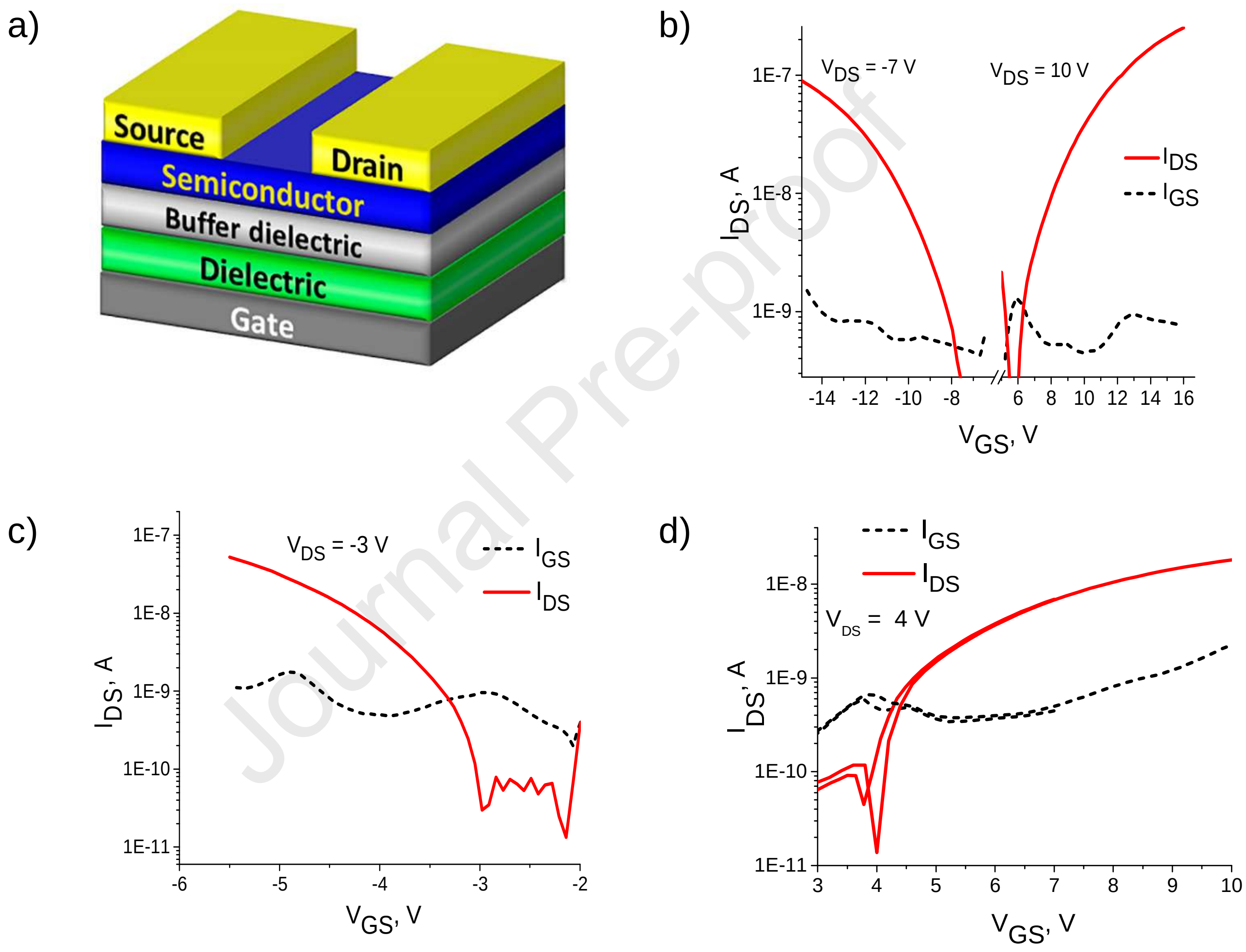

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Figure 4. Configuration of OFET devices (a) and transfer characteristics of indigoids **1** (b), **4** (c), and **8** (d) in these devices.

indigo derivatives.

Compound	Type of charge carriers	Dielectric	V_{TH} (V)*	I_{on}/I_{off}	μ ($cm^2\ V^{-1}\ s^{-1}$)**	μ_e/μ_h
1	*n*	BCB	15	10	$1.1{\times}10^{-4}$	n/a
	n	TC	7	$9{\times}10^{2}$	$4.0{\times}10^{-3}$	~1
	p	TC	-7	10	$4.7{\times}10^{-3}$	
2	*n*	AlO_x	10	10	$3.1{\times}10^{-5}$	n/a
4	*n*	TC	-3	10	$\sim 10^{-6}$	~0.001
	p	TC	4	$1{\times}10^{3}$	$3.8{\times}10^{-3}$	
5	*p*	TC	-4.5	4×10	$3.8{\times}10^{-4}$	n/a
8	*n*	TC	7.2	$1{\times}10^{2}$	$2.8{\times}10^{-4}$	n/a
9	*n*	TC	2.1	$1{\times}10^{2}$	$9.1{\times}10^{-5}$	n/a
Indigo	*n*	BCB	3.8	$3{\times}10^{2}$	$(0.8\text{-}1.5){\times}10^{-4}$	n/a
	n	TC	4.9	$4{\times}10^{3}$	$(1.0\text{-}1.3){\times}10^{-3}$	~4
	p	TC	-5.0	$2{\times}10^{2}$	$(1.0\text{-}3.0){\times}10^{-4}$	

* Threshold voltage. ** Charge carrier mobility.

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It was expected that the presence of thienyl, phenyl, or naphthyl rings in compounds **4–9** would lead to an effective ordering of the molecules in thin films resulting in improved charge transport properties. However, the acquired experimental data have not supported this suggestion. In particular, thin films of compounds **6** and **7** did not demonstrate any semiconductor properties with all the studied dielectrics. Derivative **5** exhibited low hole mobilities in OFETs (Table 2). On the contrary, 6,6'-dithienylindigo **4** turned out to be the ambipolar semiconductor on hydrocarbon dielectrics (TC), but the electron mobilities were lower by 3 orders of magnitude than the hole mobilities (Table 2, Figure 4c). Alkylditienylindigo **8** and dibenzoindigo **9** demonstrated only a poor electron mobility in combination with TC dielectric (Figure 4d), while known isomer of compound **9** showed excellent *p*-type behavior in OFETs with the mobility higher by few orders are caused by its crystal structure (see above).

The films of indigoids **1**, **3**, **4**, **5** and **7** grown on TC and BCB dielectric coatings were investigated using atomic force microscopy (AFM) (ESI, Figure S13). However, the surface topography of the films failed to explain the observed differences in the electrical performance of OFETs. For instance, indigoid **1** shows more crystalline films when it is deposited on BCB rather than on TC. However, the OFETs assembled with **1** and TC dielectric show better performance presumably due to the molecular templating effect revealed previously [41]. Surface topography of thin films of compounds **1**, **3** and **7** grown on TC dielectric looks very similar. However, no semiconductor properties were revealed for **3** and **7**, whereas **1** showed good performance in OFETs. The obtained results match our previous findings [27] suggesting that supramolecular ordering of the molecules in the films, i.e. crystal packing, is the most important factor defining the semiconductor performance of indigo derivatives in OFETs.

It should be also noted that the chemical functionalization of indigo allows one to tune electronic properties of indigo derivatives (frontier orbitals energies are given in Figure S14, ESI) and their electrical performance in OFETs. The ambipolar behavior with balanced electron and hole mobilities was clearly observed in the case of 6,6'-diiodoindigo (Figure 5). Increase in electronegativity of halogen atoms at the 6 and 6' positions as well as introduction of fluorine atoms at the 5 and 5' positions (tetrafluoroindigo) or implementation of strong electron acceptor substituents (CF_3) cause a decrease in the hole mobility down to its complete disappearance. [27] In contrast, the electron mobility only slightly depends on the chemical nature in the case of derivatives bearing two halogen substituents, but it decreases upon increasing the number of electron-withdrawing substituents (F atoms). In the case of four fluorine atoms (*i.e.*, tetrafluoroindigo), the electron mobility fell just to one half of that of 6,6'-difluoroindigo, but for the eight fluorine atoms (octafluoroindigo **2**) the mobility was lower by few orders of magnitude. The obtained results are clearly indicating the opportunities for using chemical design to tune properties of indigo-based organic semiconductor materials.

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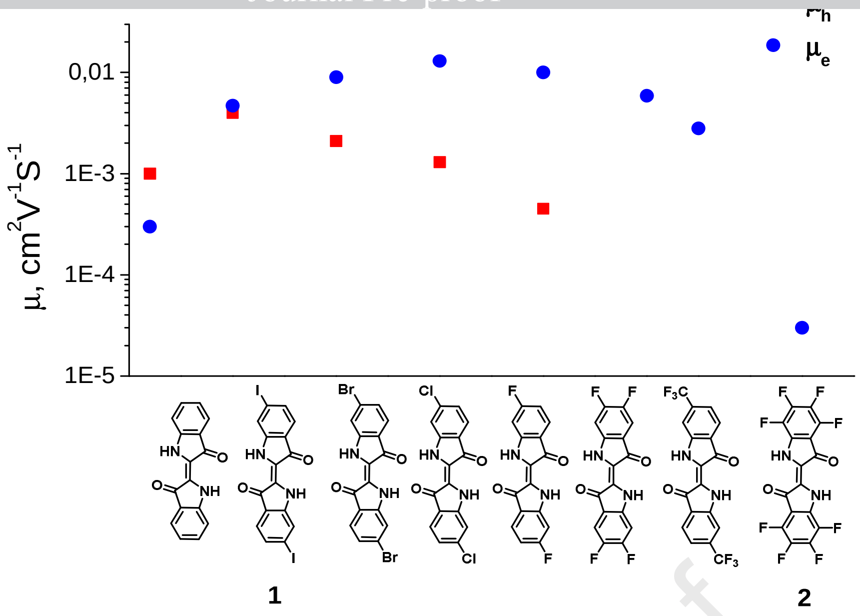

Figure 5. Effect of substituents in indigo core on electron and hole mobilities in OFETs

CONCLUSIONS

The set of novel indigo derivatives was designed following two major strategies based on: (1) considering the effects of halogen substituents used to tailor optoelectronic properties of the materials and their performance in OFET devices and (2) increasing the molecular π-conjugated system with additional aromatic rings. The first approach has revealed a well-balanced ambipolar behavior for 6,6'-diiodoindigo, which can be considered as a highly promising organic semiconductor. On the contrary, the introduction of multiple halogen atoms with stronger electron-withdrawing properties suppresses hole transport and, unfortunately, deteriorates also electron mobility lie observed in case of octafluoroindigo and octachloroindigo. The second approach provided a more diverse series of the indigo derivatives. The introduction of thiophene and phenyl substituents at positions 6 and 6' of indigo led to the predominance of hole transport due to the donor properties of these groups. Another compound, *z*-shaped dibenzoindigo demonstrated a poor performance in OFET devices as compared to both parent indigo and linear dibenzoindigo due to the strong displacement of the molecules with respect to each other and a reduced intermolecular overlap of the boundary orbitals. These revealed structure-properties

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ith improved electronic properties for sustainable and biocompatible organic electronics.

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HIGHLIGHTS

1. Nine novel indigo derivatives are designed, synthesized and chracterized.
2. Single crystal structures are obtained for three indigo derivatives
3. A well-balanced ambipolar behavior in OFETs is found for 6,6’-diiodoindigo.
4. Semiconductor performance of halogenated indigoids correlates with their structures

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Declaration of interests

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

☐The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

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