

Versatile Strategy to Develop Sequence-Defined Conjugated Macromolecules: A Powerful Tool toward Tunable Optoelectronic Properties

Wout Milis, Janine Peeters, Robin Erkens, Julien De Winter, Pascal Gerbaux, and Guy Koeckelberghs*



Cite This: *ACS Macro Lett.* 2024, 13, 1293–1303



Read Online

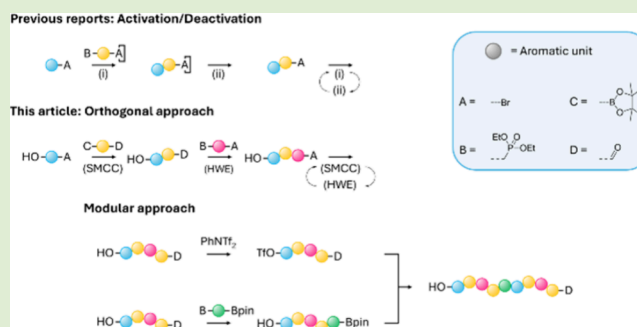
ACCESS |

Metrics & More

Article Recommendations

Supporting Information

ABSTRACT: Conjugated sequence-defined polymers represent a cutting-edge area of polymer science, merging the precision of biological macromolecules with the versatility of synthetic polymers and the unique properties of conjugated systems. While early reports focused on activation/deactivation strategies, this Letter presents the first orthogonal approach to developing sequence-defined conjugated macromolecules (CMs), incorporating a new monomer at each reaction step. In CMs, the primary monomer sequence meticulously determines the optoelectronic properties. Step-by-step, features such as structural defects, chain length, dispersity, functional groups, topology, and monomers used in the backbone are carefully considered and controlled, with optical data provided to support the necessity of sequence-defined approaches in CMs. Additionally, a pioneering and repeatable modular approach is introduced, connecting different orthogonally developed sequences. This method enhances efficiency and accelerates the synthesis process, facilitating comprehensive structure–property analyses and paving the way for tunable materials with record-breaking properties.



Conjugated macromolecules (CMs) are incredibly interesting because of the processability and versatility of polymers combined with the electronic characteristics of inorganic semiconductors.^{1,2} Their remarkable optoelectronic features make CMs highly attractive for various applications such as OFETs,^{3,4} OLEDs,^{3,5} photovoltaic cells,^{6,7} thermoelectrics,^{8,9} and in nonlinear optics.¹⁰ However, the properties of CMs are determined and severely hampered by a number of factors such as structural defects, dispersity, chain length, functional end-groups, topology, and monomers used in the backbone. As a result, precision control of the monomer sequence is crucial in tuning the optoelectronic properties.^{1,2} An impressive example of this precision synthesis is observed in biopolymers such as DNA and peptides. Depending on the sequence of the nucleobases or amino acids, the structure serves a totally different purpose. This observation in nature sparked scientists' curiosity to mimic the absolute control of these biopolymers.

For nonconjugated polymers, this journey began with Merrifield developing a method making peptides easily accessible and paving the way toward a new field of research, i.e., sequence-defined macromolecules.¹¹ In the past decades, the field of polymer science witnessed a surge of interest concerning the synthesis of polymers with precisely defined monomer sequences. Ever since, a plethora of synthetic strategies have been developed to obtain sequence-defined

structures. One notable approach is based on single-unit monomer insertions (SUMIs).^{12–16} This strategy aims to reduce the reactivity of the growing chain ends commonly observed in classical reversible deactivation radical polymerizations. While these methods focus on controlled radical polymerizations, alternative approaches involve one-by-one iterative syntheses typically following an activation/deactivation pattern^{17–20} or an orthogonal approach.^{21–25}

Contrary to nonconjugated polymers, progress in conjugated systems is limited. Transition-metal-catalyzed transfer polycondensation has been widely studied but is not the holy grail.^{26,27} Inevitably associated with this controlled polymerization is the molar mass distribution, incorporation of defects, and no absolute control of end-groups nor of precise monomer sequence, which all exert a substantial impact on the properties. The past few years, appealing examples of sequence-defined conjugated polymers have been published. However, these approaches use the activation/deactivation method either by converting a functional end-group to another

Received: August 5, 2024

Revised: September 4, 2024

Accepted: September 5, 2024

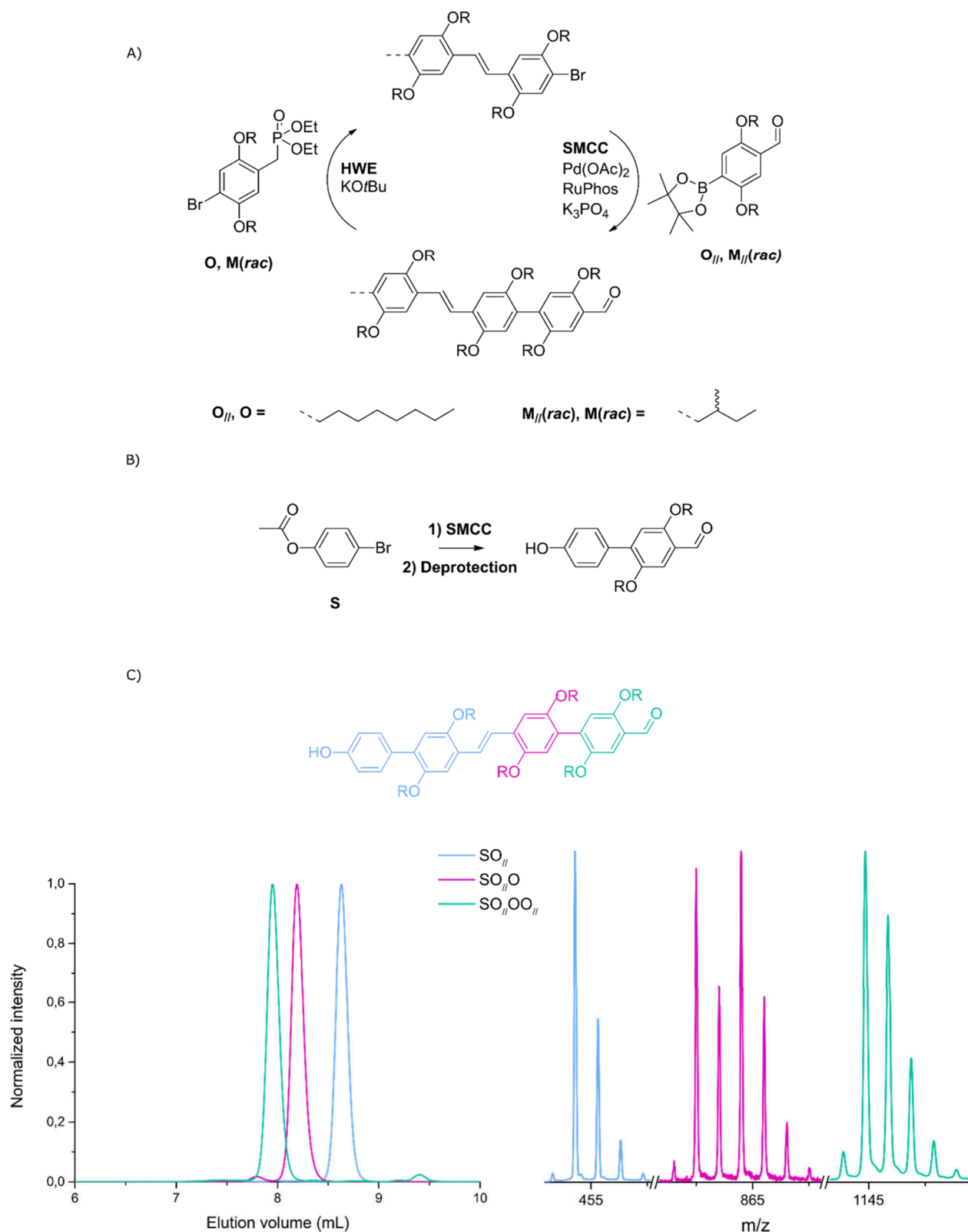


Figure 1. (A) Illustration of the orthogonal reaction scheme with monomers used. The // denotes where the aldehyde monomer/double bond is incorporated in the backbone. (B) Illustration of the starting molecule with a deprotection after the first coupling. (C) The backbone of the different tetramers developed and SEC (left) and MALDI-HRMS (right) graph of the $SO_{//}OO_{//}$ sequence.

functionality,^{28–30} by implementing protection/deprotection strategies,^{31–37} or by temperature controlling.^{38,39} Compared to nonconjugated systems, there is a lack of orthogonal alternatives.

In this study, a novel and expeditious procedure is revealed based on orthogonal reactions incorporating a different monomer in each reaction step. Alongside the utilization of diverse building blocks to synthesize different sequences, end-

groups and topology are also varied, and their importance is demonstrated. Moreover, a pioneering and repeatable modular approach is proposed, employing the frequently observed method of activation/deactivation to connect different orthogonally developed oligomer segments. As a consequence, a material can be improved by resynthesizing only one specific segment rather than the entire macromolecule, thus facilitating the overall synthesis.

Step-by-step, all features influencing the optoelectronic properties will be considered and controlled. First, a proof of principle is provided to verify the suggested approach, which confirms the uniformity of the sequence, the absence of defects, and control of functional groups. Then, chiral monomers are applied to investigate the chiroptical properties and aggregation behavior depending on the monomer position within the sequence. Next, a multifunctional monomer is incorporated into the backbone, establishing topological changes that influence the conjugation length. In addition, a new monomer building block is introduced, modifying the topology and conjugation length without disrupting the latter. Finally, the novel modular approach is revealed, showing its power to boost proper structure–property analyses

To establish an orthogonal approach, two distinct non-interfering coupling reactions are essential. Consequently, it is imperative to employ AB and CD functionalized monomers whereby the A functionality exclusively reacts with function D, while functionality B solely reacts with function C. Frequently used reactions to link aromatic molecules are cross-coupling reactions. These reactions are metal-catalyzed and typically involve an aryl halide and an organometallic compound. Because of the nature of the required reagents, such as aryl halides, only one cross-coupling reaction can be applied. Considering the wide applicability of the Suzuki–Miyaura cross coupling (SMCC) and the inexpensive and nontoxic nature of its reagents, this reaction was selected.^{40,41} For the second coupling reaction, three different reactions were evaluated as potential candidates (SI S6) among which the Horner–Wadsworth–Emmons (HWE) emerged as the most reliable.⁴²

Due to the combination of the SMCC and HWE reactions, monomers featuring a bromide function and a phosphonate group on one hand and a boronic ester and an aldehyde function on the other hand have been devised. Both monomeric units follow a synthetic procedure based on well-known reactions with a shared intermediate (SI S11). The applied reaction sequence consists of a Williamson ether synthesis of hydroquinone followed by dibromination using bromine (Br_2). Subsequently, one bromide function is converted to an aldehyde with *n*-BuLi, DMF, and H^+ in a Bouveault reaction to obtain the intermediate, of which both desired structures are generated. On one hand, the bromide function can be substituted to a boronic ester via Miyaura borylation ($\text{O}_{//}$). On the other hand, the aldehyde can be reduced to an alcohol that can be converted into a chlorine function. The so-obtained benzylic chloride is subjected to the Arbuzov reaction, affording the requisite phosphonate (O).

In addition to the monomers required to enlarge the oligomer, a premeditated starting molecule (S) has been designed, from which the oligomers are synthesized. This starting molecule possesses a bromide functionality to ensure the unidirectional growth, but also a (protected) alcohol function providing a versatile end-group with numerous postpolymerization possibilities. The design of this compound

is the result of a brief study aimed at identifying the optimal starting molecule (SI S9). To enhance the solubility, and thus the kinetics of the first SMCC reaction, the hydroxyl group is temporarily protected as an acetate. In order to prevent any side reactions during subsequent HWE chain elongation, the hydroxyl group is deprotected after the first coupling reaction (Figure 1).

After optimization of both the monomer synthesis and coupling reactions, the first conjugated oligomer developed in an orthogonal approach is synthesized ($\text{SO}_{//}\text{OO}_{//}$). Not only are we able to develop a tetramer in 79.4% overall yield but also the purification proves to be fairly easy using crystallizations or precipitations only. Besides the starting molecule, which does not possess any side chains, the used monomers all possess octyl side chains because of the easier monomer synthesis owing to the linear character. However, to extend the potential of the new orthogonal approach, monomers with racemic 2-methylbutyl side chains are synthesized, resulting in two sets of two monomers ($\text{O}_{//}$, O , $\text{M}_{//}(\text{rac})$, $\text{M}(\text{rac})$). To show the versatility of the method, three additional oligomers with different sequences but identical compositions are synthesized ($\text{SM}_{//}\text{OO}_{//}(\text{rac})$, $\text{SO}_{//}\text{OM}_{//}(\text{rac})$, and $\text{SO}_{//}\text{MO}_{//}(\text{rac})$).

As a result, four different aspects that determine the properties of conjugated polymers are controlled. Perfect end-group fidelity is realized with the hydroxyl group and the bromide function or aldehyde at the extremities of the macromolecule. In addition, classic characterization techniques such as SEC, ^1H NMR, and MALDI-HRMS unambiguously confirm the obtention of perfectly defined monomer sequences and defect-free structures with defined chain lengths.

Chirality. Next, the chain length of the oligomers is increased from tetramer to hexamer, and a monomer with a chiral (*S*)-2-methylbutyl side chain is used ($\text{M}_{//}(\text{S})$). This chiral monomer is combined with the regular octyl side chain monomers to develop two chiral hexamers with a linear backbone ($\text{SO}_{//}\text{OM}_{//}\text{OM}_{//}(\text{S})$ and $\text{SM}_{//}\text{OO}_{//}\text{OM}_{//}(\text{S})$), affording two optical isomers differing in sequence.

With six previous different oligomers (racemic and chiral sequences), the first optical observations can be drawn regarding the influence of monomers used, chain length, and end-groups via UV–vis and fluorescence spectroscopies. As expected, diversification of monomers by using different side chains does not significantly affect the optical properties significantly. Therefore, the spectroscopic results of these phenyl-only oligomers are consistent and remain unchanged independent of the sequence.

As the oligomer progresses from dimer to hexamer, the conjugation length increases stepwise because of the enhanced delocalization and the increasing number of π -electrons, facilitated by the additional aromatic ring. The redshift induced by this extra monomer depends on two factors, namely, the planarity of the backbone and the functional end-groups. Following a HWE reaction (odd sequences), a vinylene bond between two phenyl rings is incorporated, leading to a planar conformation. In contrast to the HWE reaction, the direct biaryl bond after an SMCC reaction (even sequences) provokes a moderate rotation between the consecutive aromatic rings due to steric hindrance. Based on these two aspects, a more significant red-shift is expected after a HWE reaction versus after an SMCC reaction. However, the push–pull system established within the oligomer following an SMCC reaction causes a strong redshift, highlighting the

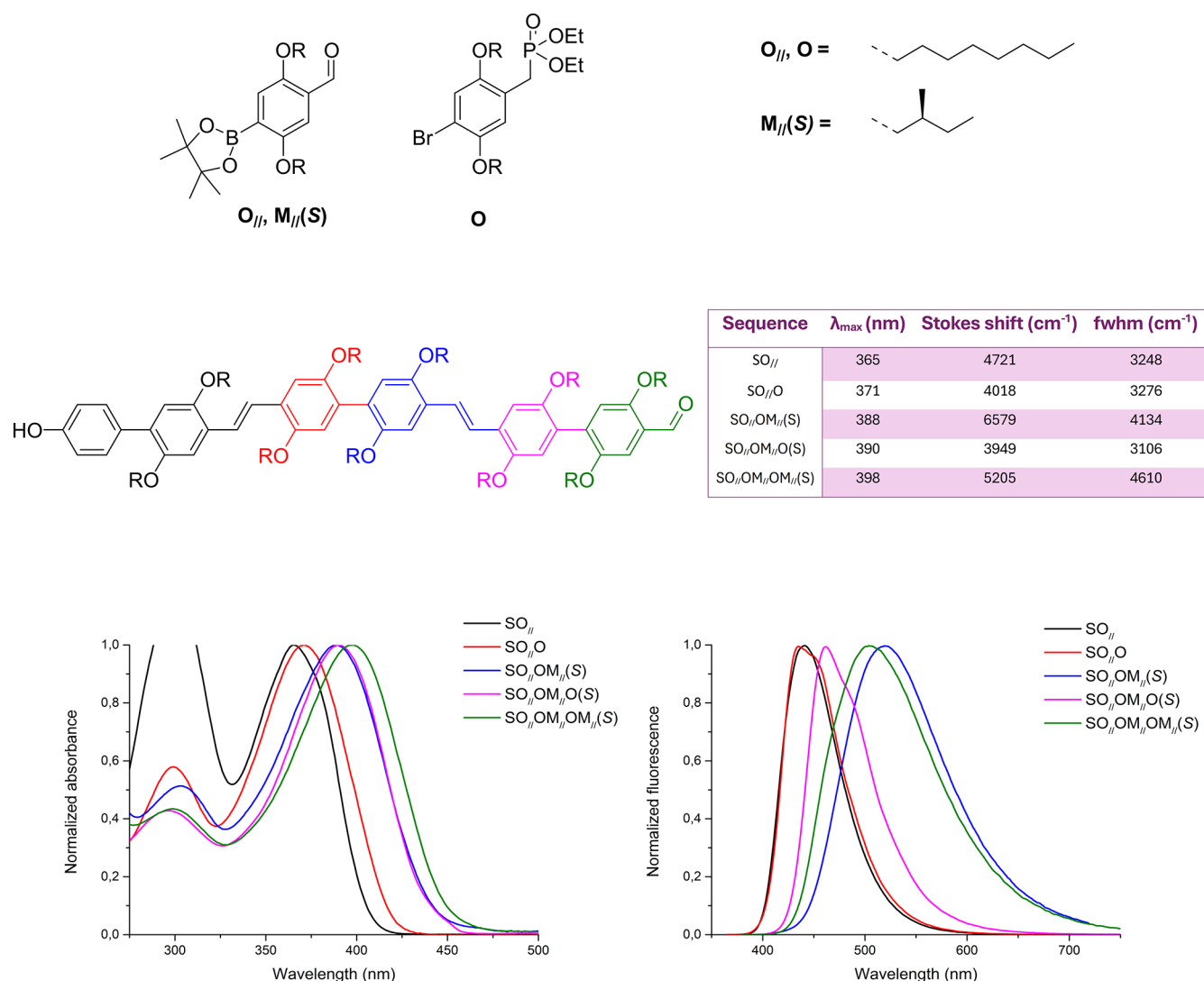


Figure 2. Illustration of the monomers used to develop linear chiral hexamers, with the backbone shown in the middle. At the bottom, a UV–vis spectrum of one hexamer on the left and the corresponding fluorescence spectrum on the right, both measured in CHCl_3 solution. In the table the λ_{\max} , Stokes shift, and fwhm of a hexamer series are shown.

importance of functional end-groups on the properties of conjugated macromolecules (Figure 2).

In the fluorescence measurements, the parameters of interest are the Stokes shift and the full width at half-maximum (fwhm) which provide information about the rigidity of the conjugated backbone. When both values are relatively high, it implies that the structures are rather flexible and vice versa. After a HWE reaction (odd sequences), both numbers tend to be relatively small, while after an SMCC reaction (even sequences), the opposite is observed. This makes sense because an SMCC introduces a biphenyl structure, reducing the overall rigidity, while after a HWE reaction a more planar vinylenic structure is incorporated, enhancing the rigidity. However, compared to literature data where fwhm of ca. 1200 cm^{-1} are observed, our oligomers appear to be fairly flexible.^{43,44} Besides these intriguing results in UV–vis and fluorescence spectroscopies, implementing chiral monomers permits the study of the chiroptical properties. Circular dichroism (CD) is a widely applied technique in conjugated systems and offers the possibility of analyzing the accompanying aggregation process. This aggregation can be induced in several ways, of which the

most frequently used method is a stepwise addition of a nonsolvent to an oligomer solution.

Experiments are performed in $2 \times 10 \text{ mm}$ quartz cuvettes with 70% of nonsolvent composed of different ratios of methanol and water, while isopropanol is used as good solvent. Unfortunately, both hexamers did not show any CD signal, although the scattering observed in the UV–vis spectra clearly indicates aggregate formation (SI 165). Note that the hexamers do not appear as clear solids in their pure form but rather in a glassy amorphous state. Therefore, the corresponding enantiomeric tetramers ($\text{SM}_{//}\text{OO}_{//}(\text{S})$ and $\text{SO}_{//}\text{OM}_{//}(\text{S})$) are investigated as they do appear as clear powders (Figure 3). Interestingly, the CD intensities are different, and the signs of both signals are opposite, which unambiguously proves the importance of the monomer sequence on the properties in conjugated macromolecules.

Topology. A next step in justifying the versatility of the newly revealed approach consists of introducing a multifunctional monomer into the sequence. This will vary the topology and is realized by the development of V_2 which contains two bromide functions to prolong the oligomer (Figure 4). This trifunctional monomer is combined with the linear octyl

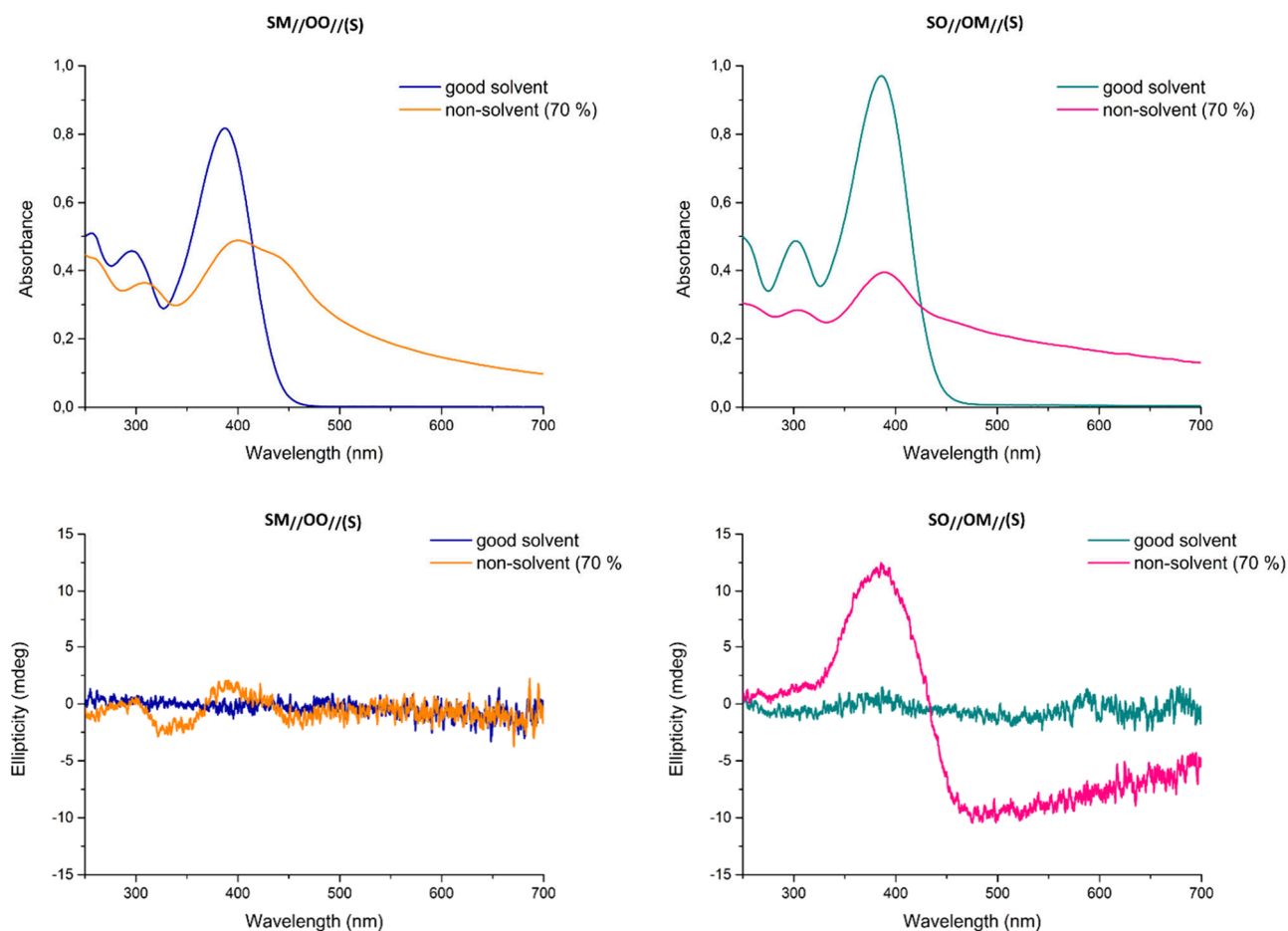


Figure 3. UV-vis (top) and CD (bottom) spectra of two chiral tetramers ($\text{SM}_{//}\text{OO}_{//}(\text{S})$ (left) and $\text{SO}_{//}\text{OM}_{//}(\text{S})$ (right)). The good solvent is IPA, and the nonsolvent is MeOH/H₂O in a 7/3 ratio added to a percentage of 70%.

monomers, as well as the chiral monomer used earlier. As a result, three different structures are synthesized: two isomeric hexamers with the trifunctional monomer at the fifth position ($\text{SM}_{//}\text{OO}_{//}\text{V}_2\text{M}_{//}(\text{S})$ and $\text{SO}_{//}\text{OM}_{//}\text{V}_2\text{M}_{//}(\text{S})$) and one pentamer with the branching molecule at the third position ($\text{SO}_{//}\text{V}_2\text{M}_{//}\text{O}(\text{S})$).

Again, the optical properties of both branched hexamers are in agreement, making the discussion applicable for both. In the hexamer structures, the UV-vis results are in line with the results of linear equivalents up to the level of the pentamer. However, a blue shift of λ_{max} is observed for the hexamers owing to the meta orientation of V_2 , which disrupts the conjugation of the oligomer backbone. Because of the branching molecule, the structure should not be seen as one single oligomer but rather as a set of one pentamer and two dimers, reducing the overall conjugation length. The same story holds for the pentamer $\text{SO}_{//}\text{V}_2\text{M}_{//}\text{O}(\text{S})$. Up to the trimer, the results are analogous; the tetramer has no improved conjugation length; and for the pentamer only a slight increase can be noticed.

The trend in the fluorescence results is also comparable to the data acquired for the linear counterparts. In the branched hexamer structures, however, the shift toward lower wavelength has the same origin as in the UV-vis results; the structure should not be perceived as one single oligomer but rather as a set of one pentamer and two dimers. The same story holds for $\text{SO}_{//}\text{V}_2\text{M}_{//}\text{O}(\text{S})$, where a clear shoulder is observed which closely resembles a combination of the

corresponding dimer and trimer fluorescence. Note that the $\text{SO}_{//}\text{V}_2\text{M}_{//}(\text{S})$ signal is, due to normalization, out of proportion, as this sequence did not appear to be fluorescent.

Likewise for the linear hexamers, solvatochromism experiments are conducted on the branched sequences to study the CD signal and accompanying aggregation process. Again, both branched hexamers did not show any CD signal, although scattering was observed in UV-vis. The reason might be the same as with the linear hexamers, as the branched hexamers also occur as viscous oils. Therefore, the same experiment was not performed on the branched pentamer $\text{SO}_{//}\text{V}_2\text{M}_{//}\text{O}(\text{S})$ as this was even more oil-like.

Bandgap Modification. To achieve a considerable impact on the optical properties, the bandgap of the oligomer backbone must be adjusted more significantly. While varying the alkoxy side chain has a negligible effect on the bandgap, substantial modification can be achieved with a new monomer building block. Phenanthrene is an intriguing alternative not only due to its different aromaticity but also because the position of the functional groups can be deliberately chosen. Instead of functionalized phenanthrene on the 2- and 7-position resulting in a linear backbone, functionalized phenanthrene on the 3- and 6-position introduces a bend of 120° along the backbone. Consequently, this modifies the topology more subtly without disrupting the conjugation within the oligomer. A new pair of phenanthrene monomers is synthesized with an identical combination of functional groups as the phenylene duplicates (**P** and **P'**), to develop three new

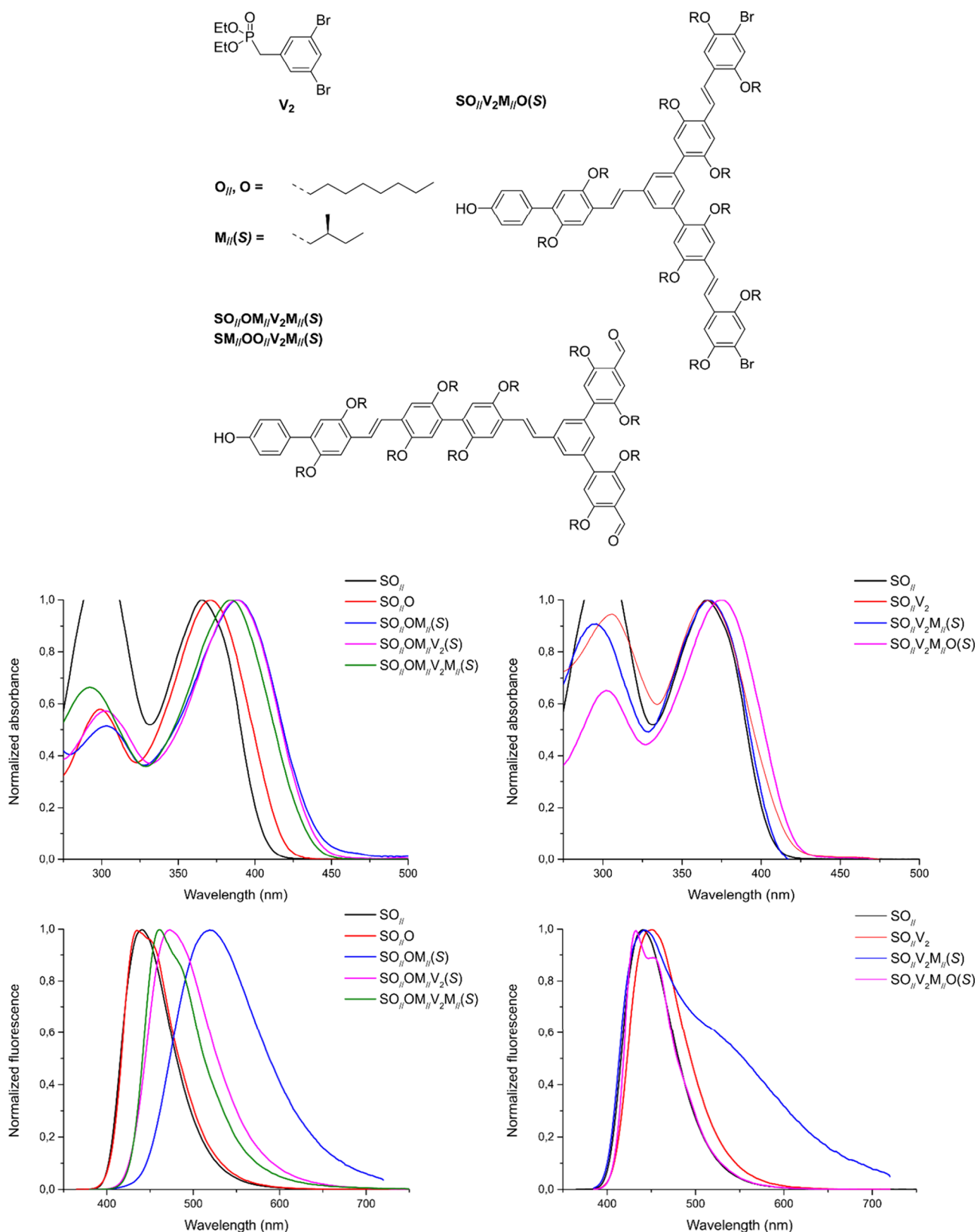


Figure 4. Top: the chemical structures of the branching molecule V_2 and the backbone of the pentamer with the branching molecule on the 3rd position and the backbone of the hexamer with the branching molecule on the 5th position. Bottom: UV-vis (top) and fluorescence (bottom) spectra, measured in $CHCl_3$ solution, of a hexamer with V_2 at the 5th position (left) and pentamer with V_2 at the 3rd position (right).

oligomers differing in monomer sequences ($SP_{//}OO_{//}$, $SO_{//}PO_{//}$, and $SO_{//}OP_{//}$) (Figure 5).

When observing the optical results in-depth, not only the shape but also the position of the spectra are different. The wavelengths of maximum absorbance for the dimer and trimers

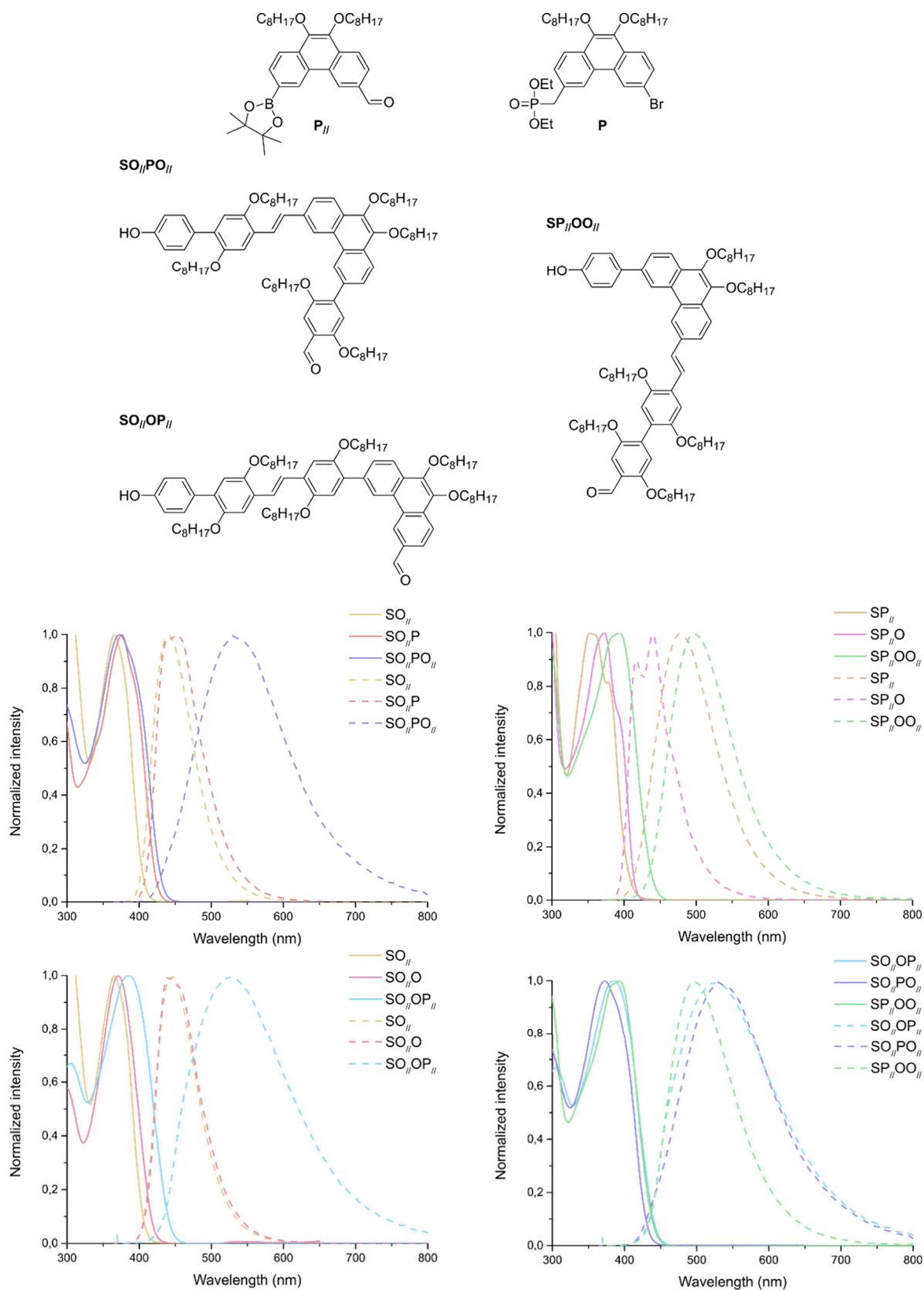


Figure 5. Synthesized phenanthrene monomers on top with the three different oligomers containing a phenanthrene. Bottom: UV-vis (solid line) and fluorescence (dashed line) of the oligomers were measured in $CHCl_3$ solution. Right bottom: corner comparison of the UV-vis and fluorescence data of the three tetramers.

are comparable to those of the phenyl oligomers, while the tetramers show a more diverse range of λ_{max} . Also the

fluorescence data is different with remarkable characteristics. First of all, the $SP_{//}$ dimer emission band is at a significantly

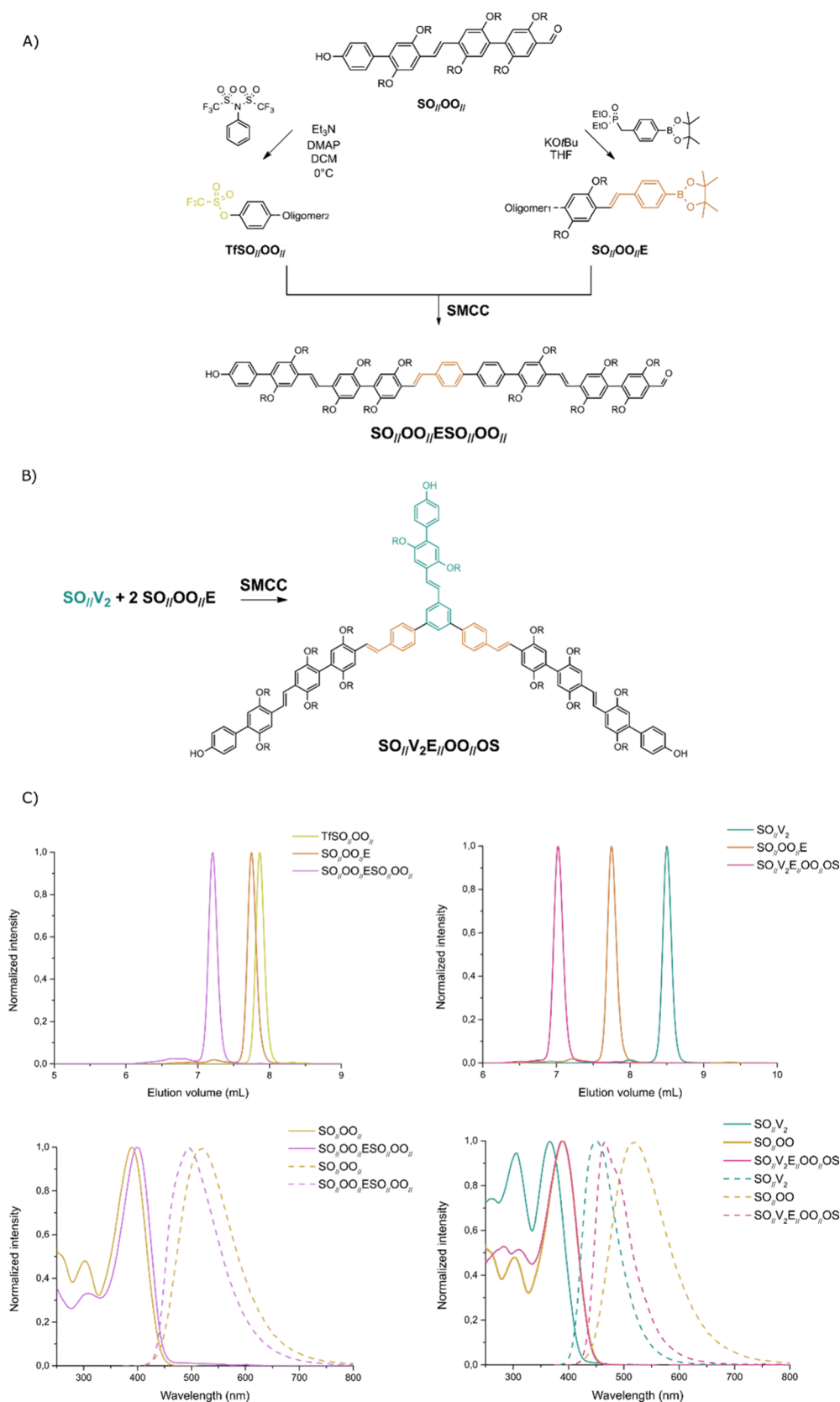


Figure 6. A) Synthesis of the different oligomer blocks based on the SO_n/OO_n sequence with the modular developed $\text{SO}_n/\text{OO}_n/\text{ESO}_n/\text{OO}_n$ as result. B) The modular approach applied on SO_nV_2 . C) SEC data (top) and UV-vis (bottom, solid line) and fluorescence data (bottom, dashed line), measured in CHCl_3 solution, of the regarding modular sequences.

lower energy than the phenylene equivalents. The emission band of the successive SP_n/O trimer shifts to a lower

wavelength, indicating a less conjugated structure than the dimer. However, both trimers SP_n/O and SO_n/P emit at higher

wavelengths in comparison to the phenyl analogues. This might demonstrate that phenanthrene enhances the conjugation more significantly in the excited state. A noteworthy result is the apparent mirror image between the absorbance and emission of the tetramers (Figure 5, bottom right). The sequence absorbing at the lowest wavelength tends to emit at the highest wavelength. Contrarily, the sequence absorbing at the highest wavelength seems to emit at the lowest wavelength.

Modular Approach. Previous results already show the importance of a sequence-defined synthesis for conducting accurate structure–property analyses. Resynthesizing entire oligomers to adjust the monomer sequence at only a few positions requires a tremendous amount of additional work. To tackle this drawback, a modular approach allows us to rapidly perform a structure–property analysis. To achieve this theory, the activation/deactivation (protection/deprotection) method mentioned in the introduction is applied in combination with orthogonal oligomer synthesis. As discussed earlier, the presence of the hydroxyl group at the start of the oligomer allows the possibility to conduct postpolymerization reactions. Considering this, a novel type of monomer is designed to serve as an end-cap molecule. This molecule will end functionalize the oligomer with a different functional group than the usual bromide or aldehyde function which is required for the orthogonal approach. More precisely, the hydroxyl group can be converted into a pseudohalide, such as a triflate group, and a phosphonate-boronic ester molecule (**E**) is developed as an end-capper (Figure 6). This enables the linkage of two distinct oligomers, one with the end-cap molecule and one with a pseudohalide, via an SMCC reaction. As a result, different oligomer segments can be synthesized simultaneously, accelerating the synthesis of a predetermined sequence. Note that this is not limited to the coupling of only two oligomers, but it can be repeatedly performed. The resulting coupled oligomer again possesses a hydroxyl group and an aldehyde able to be converted or end-capped, respectively. To demonstrate this modular approach, two different structures are designed ($\text{SO}_{//}\text{OO}_{//}\text{ESO}_{//}\text{OO}_{//}$ and $\text{SO}_{//}\text{V}_2\text{E}_{//}\text{OO}_{//}\text{OS}$). Again, both sequences are characterized with classic characterization techniques, showing perfectly defined sequences and defect-free structures with precisely known chain lengths. In addition, the optical spectra undoubtedly show how connecting different segments influences the properties, thus showing the importance of this modular approach.

In this study, an orthogonal approach to synthesizing sequence-defined conjugated macromolecules based on the SMCC and HWE reactions is established. The combination of these reactions enables the synthesis of defect-free and precisely defined sequences of conjugated macromolecules. The proof of principle is demonstrated by synthesizing oligomers with different sequences and compositions, utilizing monomers with linear, racemic, and chiral side chains. Optical properties of these oligomers are analyzed by using UV–vis and fluorescence spectroscopies, revealing insights into the effects of chain lengths and end-groups on the conjugation and rigidity. The chiroptical properties are studied with circular dichroism, showing the different results of sequences with an equal monomer composition. Additionally, the study explored the use of a multifunctional monomer to vary the topology, showing consistent optical properties and demonstrating the robustness of the approach. Further, a new aromatic monomer is incorporated to modify the bandgap more significantly and

subtly vary the topology without disrupting the conjugation. Again, the spectroscopic results emphasize the importance of defined monomer sequences as different results are obtained with the same monomer compositions. Finally, a modular synthesis strategy is introduced, allowing for the rapid assembly of oligomers by linking distinct segments. This approach significantly expedited the synthesis process and provided a pathway for detailed structure–property analyses. The successful implementation of this orthogonal approach and modular strategy highlights its potential for creating well-defined conjugated macromolecules with tailored properties for advanced optical material applications.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsmacrolett.4c00526>.

Materials, instrumentation, development, orthogonal procedure, experimental synthesis and methods, and additional tables and figures, including NMR, SEC, HRMS, UV–vis, fluorescence, and CD spectra (PDF)

■ AUTHOR INFORMATION

Corresponding Author

Guy Koeckelberghs – Laboratory for Polymer Synthesis, KU Leuven, B-3001 Heverlee, Belgium; orcid.org/0000-0003-1412-8454; Email: guy.koeckelberghs@kuleuven.be

Authors

Wout Milis – Laboratory for Polymer Synthesis, KU Leuven, B-3001 Heverlee, Belgium

Janine Peeters – Laboratory for Polymer Synthesis, KU Leuven, B-3001 Heverlee, Belgium

Robin Erkens – Laboratory for Polymer Synthesis, KU Leuven, B-3001 Heverlee, Belgium

Julien De Winter – Organic Synthesis and Mass Spectrometry Laboratory, Center of Innovation and Research in Materials and Polymers (CIRMAP), University of Mons, B-700 Mons, Belgium; orcid.org/0000-0003-3429-5911

Pascal Gerbaux – Organic Synthesis and Mass Spectrometry Laboratory, Center of Innovation and Research in Materials and Polymers (CIRMAP), University of Mons, B-700 Mons, Belgium; orcid.org/0000-0001-5114-4352

Complete contact information is available at:

<https://pubs.acs.org/doi/10.1021/acsmacrolett.4c00526>

Author Contributions

W.M., J.P., and R.E. synthesized all the compounds, conducted structural characterization studies, and performed all the optical measurements. J.W. executed and analyzed the MALDI-MS measurements. P.G. provided critical feedback on the manuscript, and G.K. supervised the project. All authors have given approval to the final version of the manuscript. CRediT: Wout Milis data curation, formal analysis, investigation, supervision, writing - original draft; Janine Peeters data curation, formal analysis, investigation, writing - review & editing; Robin Erkens data curation, formal analysis, investigation, writing - review & editing; Guy Koeckelberghs conceptualization, funding acquisition, project administration, supervision, writing - review & editing.

Notes

The authors declare no competing financial interest.

REFERENCES

- (1) Müllen, K.; Scherf, U. Conjugated Polymers: Where We Come From, Where We Stand, and Where We Might Go. *Macromol. Chem. Phys.* John Wiley & Sons, Ltd., 2023; p 2200337.
- (2) Swager, T. M. 50th Anniversary Perspective: Conducting/Semiconducting Conjugated Polymers. A Personal Perspective on the Past and the Future **2017**, 50 (13), 4867–4886.
- (3) Sirringhaus, H. 25th Anniversary Article: Organic Field-Effect Transistors: The Path Beyond Amorphous Silicon. *Adv. Mater.* **2014**, 26 (9), 1319–1335.
- (4) Allard, S.; Forster, M.; Souharce, B.; Thiem, H.; Scherf, U. Organic Semiconductors for Solution-Processable Field-Effect Transistors (OFETs). *Angew. Chem., Int. Ed.* **2008**, 47 (22), 4070–4098.
- (5) Wei, Q.; Ge, Z.; Voit, B. Thermally Activated Delayed Fluorescent Polymers: Structures, Properties, and Applications in OLED Devices. *Macromol. Rapid Commun.* John Wiley & Sons, Ltd., 2019; p 1800570.
- (6) Facchetti, A. π -Conjugated Polymers for Organic Electronics and Photovoltaic Cell Applications. *Chem. Mater.* **2011**, 23 (3), 733–758.
- (7) Coakley, K. M.; McGehee, M. D. Conjugated Polymer Photovoltaic Cells. *Chem. Mater.* **2004**, 16 (23), 4533–4542.
- (8) Yao, C. J.; Zhang, H. L.; Zhang, Q. Recent Progress in Thermoelectric Materials Based on Conjugated Polymers. *Polymers* **2019**, Vol. 11, Page 107 **2019**, 11 (1), 107.
- (9) Wang, S.; Zuo, G.; Kim, J.; Sirringhaus, H. Progress of Conjugated Polymers as Emerging Thermoelectric Materials. *Prog. Polym. Sci.* **2022**, 129, No. 101548.
- (10) Van Cleuvenbergen, S.; Asselberghs, I.; Vanormelingen, W.; Verbiest, T.; Franz, E.; Clays, K.; Kuzyk, M. G.; Koeckelberghs, G. Record-High Hyperpolarizabilities in Conjugated Polymers. *Journal of Materials Chemistry C* **2014**, 2 (23), 4533–4538.
- (11) Merrifield, R. B. Solid Phase Peptide Synthesis. I. The Synthesis of a Tetrapeptide. *J. Am. Chem. Soc.* **1963**, 85 (14), 2149–2154.
- (12) Vandenberg, J.; Reekmans, G.; Adriaenssens, P.; Junkers, T. Synthesis of Sequence-Defined Acrylate Oligomers via Photo-Induced Copper-Mediated Radical Monomer Insertions. *Chemical Science* **2015**, 6 (10), 5753–5761.
- (13) Xu, J.; Fu, C.; Shanmugam, S.; Hawker, C. J.; Moad, G.; Boyer, C. Synthesis of Discrete Oligomers by Sequential PET-RAFT Single-Unit Monomer Insertion. *Angewandte Chemie - International Edition* **2017**, 56 (29), 8376–8383.
- (14) Xu, J. Single Unit Monomer Insertion: A Versatile Platform for Molecular Engineering through Radical Addition Reactions and Polymerization. *Macromolecules* **2019**, 52 (23), 9068–9093.
- (15) Houshyar, S.; Keddie, D. J.; Moad, G.; Mulder, R. J.; Saubern, S.; Tsanaktsidis, J. The Scope for Synthesis of Macro-RAFT Agents by Sequential Insertion of Single Monomer Units. *Polym. Chem.* **2012**, 3 (7), 1879–1889.
- (16) Oh, D.; Ouchi, M.; Nakanishi, T.; Ono, H.; Sawamoto, M. Iterative Radical Addition with a Special Monomer Carrying Bulky and Convertible Pendant: A New Concept toward Controlling the Sequence for Vinyl Polymers. *ACS Macro Lett.* **2016**, 5 (6), 745–749.
- (17) Dong, R.; Liu, R.; Gaffney, P. R. J.; Schaeperstoens, M.; Marchetti, P.; Williams, C. M.; Chen, R.; Livingston, A. G. Sequence-Defined Multifunctional Polyethers via Liquid-Phase Synthesis with Molecular Sieving. *Nat. Chem.* **2019**, 11 (2), 136–145.
- (18) Solleder, S. C.; Zengel, D.; Wetzels, K. S.; Meier, M. A. R. A Scalable and High-Yield Strategy for the Synthesis of Sequence-Defined Macromolecules. *Angewandte Chemie - International Edition* **2016**, 55 (3), 1204–1207.
- (19) Barnes, J. C.; Ehrlich, D. J. C.; Gao, A. X.; Leibfarth, F. A.; Jiang, Y.; Zhou, E.; Jamison, T. F.; Johnson, J. A. Iterative Exponential Growth of Stereo- and Sequence-Controlled Polymers. *Nature Chemistry* **2015**, 7 (10), 810–815.
- (20) Takizawa, K.; Tang, C.; Hawker, C. J. Molecularly Defined Caprolactone Oligomers and Polymers: Synthesis and Characterization. *J. Am. Chem. Soc.* **2008**, 130 (5), 1718–1726.
- (21) Pfeifer, S.; Zarafshani, Z.; Badi, N.; Lutz, J. F. Liquid-Phase Synthesis of Block Copolymers Containing Sequence-Ordered Segments. *J. Am. Chem. Soc.* **2009**, 131 (26), 9195–9197.
- (22) Solleder, S. C.; Meier, M. A. R. Sequence Control in Polymer Chemistry through the Passerini Three-Component Reaction. *Angewandte Chemie - International Edition* **2014**, 53 (3), 711–714.
- (23) Porel, M.; Alabi, C. A. Sequence-Defined Polymers via Orthogonal Allyl Acrylamide Building Blocks Scheme 1. Fluorous Assisted Sequence Control via Allyl Acrylamides and Dithiols. *J. Am. Chem. Soc.* **2014**, 136, 13162.
- (24) Zuckermann, R. N.; Kerr, J. M.; Kent, S. B. H.; Moos, W. H. Efficient Method for the Preparation of Peptoids [Oligo(N-Substituted Glycines)] by Submonomer Solid-Phase Synthesis. *J. Am. Chem. Soc.* **1992**, 114, 10646–10647.
- (25) Espeel, P.; Carrette, L. L. G.; Bury, K.; Capenberghs, S.; Martins, J. C.; Duprez, F. E.; Madder, A. Multifunctionalized Sequence-Defined Oligomers from a Single Building Block. *Angewandte Chemie - International Edition* **2013**, 52 (50), 13261–13264.
- (26) Yokoyama, A.; Miyakoshi, R.; Yokozawa, T. Chain-Growth Polymerization for Poly(3-Hexylthiophene) with a Defined Molecular Weight and a Low Polydispersity. *Macromolecules* **2004**, 37, 1169–1171.
- (27) Sheina, E. E.; Liu, J.; Iovu, M. C.; Laird, D. W.; McCullough, R. D. Chain Growth Mechanism for Regioregular Nickel-Initiated Cross-Coupling Polymerizations. *Macromolecules* **2004**, 37 (10), 3526–3528.
- (28) Yu, H.; Li, S.; Schwieter, K. E.; Liu, Y.; Sun, B.; Moore, J. S.; Schroeder, C. M. Charge Transport in Sequence-Defined Conjugated Oligomers. *J. Am. Chem. Soc.* **2020**, 142 (10), 4852–4861.
- (29) Yin, J.; Choi, S.; Pyle, D.; Guest, J. R.; Dong, G. Backbone Engineering of Monodisperse Conjugated Polymers via Integrated Iterative Binomial Synthesis. *J. Am. Chem. Soc.* **2023**, 145 (34), 19120–19128.
- (30) Norris, B. N.; Pan, T.; Meyer, T. Y. Iterative Synthesis of Heterotelechelic Oligo(Phenylene-Vinylene)s by Olefin Cross-Metathesis. *Org. Lett.* **2010**, 12 (23), 5514–5517.
- (31) Xu, C.; He, C.; Li, N.; Yang, S.; Du, Y.; Matyjaszewski, K.; Pan, X. Regio- and Sequence-Controlled Conjugated Topological Oligomers and Polymers via Boronate-Tag Assisted Solution-Phase Strategy. *Nat. Commun.* **2021**, 12 (1), 5853.
- (32) Szweda, R.; Chendo, C.; Charles, L.; Baxter, P. N. W.; Lutz, J. F. Synthesis of Oligoarylacetylenes with Defined Conjugated Sequences Using Tailor-Made Soluble Polymer Supports. *Chem. Commun.* **2017**, 53 (59), 8312–8315.
- (33) Schneider, R. V.; Waibel, K. A.; Arndt, A. P.; Lang, M.; Seim, R.; Busko, D.; Bräse, S.; Lemmer, U.; Meier, M. A. R. Sequence-Definition in Stiff Conjugated Oligomers. *Sci. Rep.* **2018**, 8 (1), 1–8.
- (34) Jørgensen, M.; Krebs, F. C. Stepwise and Directional Synthesis of End-Functionalized Single-Oligomer OPVs and Their Application in Organic Solar Cells. *J. Org. Chem.* **2004**, 69 (20), 6688–6696.
- (35) Iwadata, N.; Sugino, M. Synthesis of B-Protected β -Styrylboronic Acids via Iridium-Catalyzed Hydroboration of Alkynes with 1,8-Naphthalenediaminoborane Leading to Iterative Synthesis of Oligo(Phenylenevinylene)s. *Org. Lett.* **2009**, 11 (9), 1899–1902.
- (36) Pearson, D. L.; Schumm, J. S.; Tour, J. M. Iterative Divergent/Convergent Approach to Conjugated Oligomers by a Doubling of Molecular Length at Each Iteration. A Rapid Route to Potential Molecular Wires. *Macromolecules* **1994**, 27 (8), 2348–2350.
- (37) Schumm, J. S.; Pearson, D. L.; Tour, J. M. Iterative Divergent/Convergent Approach to Linear Conjugated Oligomers by Successive Doubling of the Molecular Length: A Rapid Route to a 128Å-Long Potential Molecular Wire. *Angewandte Chemie International Edition in English* **1994**, 33 (13), 1360–1363.
- (38) Mills, H. A.; Rahman, S.; Zigelstein, R.; Xu, H.; Varju, B. R.; Bender, T. P.; Wilson, M. W. B.; Seferos, D. S. Sequence-Defined Conjugated Oligomers in Donor-Acceptor Dyads. *J. Am. Chem. Soc.* **2023**, 145 (43), 23519–23526.

(39) Xu, H.; Ye, S.; Zhao, R.; Seferos, D. S. Homogeneous Synthesis of Monodisperse Sequence-Defined Conjugated Oligomers by Temperature Cycling. *Angew. Chem., Int. Ed.* **2022**, *61* (39), No. e202210340.

(40) Martin, R.; Buchwald, S. L. Palladium-Catalyzed Suzuki-Miyaura Cross-Coupling Reactions Employing Dialkylbiaryl Phosphine Ligands. *Acc. Chem. Res.* **2008**, *41*, 1461–1473.

(41) Miyaura, N.; Suzuki, A. Palladium-Catalyzed Cross-Coupling Reactions of Organoboron Compounds. *Chem. Rev.* **1995**, *95* (7), 2457–2483.

(42) Wadsworth, W. S.; Emmons, W. D. The Utility of Phosphonate Carbanions in Olefin Synthesis. *J. Am. Chem. Soc.* **1961**, *83* (7), 1733–1738.

(43) Koeckelberghs, G.; De Cremer, L.; Persoons, A.; Verbiest, T. Influence of the Substituent and Polymerization Methodology on the Properties of Chiral Poly(Dithieno[3,2-b:2',3'-d]Pyrrole)s. *Macromolecules* **2007**, *40* (12), 4173–4181.

(44) Ogawa, K.; Rasmussen, S. C. N-Functionalized Poly(Dithieno[3,2-b:2',3'-d]Pyrrole)s: Highly Fluorescent Materials with Reduced Band Gaps. *Macromolecules* **2006**, *39* (5), 1771–1778.