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Polyacetylenes with (hetero)aryl-, styryl-, and amino-phenothiazinyl sidechains: synthesis and photophysics†

 Wladislaw Pisetsky and Thomas J. J. Müller *

A novel generation of 7-aryl phenothiazinyl substituted polyacetylenes is readily accessible *via* controlled rhodium-catalyzed polymerization of the corresponding 3-ethynyl 7-aryl phenothiazines. The monomers are synthesized by Suzuki coupling, Heck coupling, or Buchwald–Hartwig amination, and Bestmann–Ohira reaction. This allows for the introduction of electron donating and releasing substituents with different ligation patterns. The obtained polymers display narrow molecular weight distributions, with very few exceptions, and are soluble in many organic solvents. The photophysical properties of novel monosubstituted polyacetylenes and corresponding monomers were compared. While the monomers exhibit strong emission in solution with quantum yields of up to 0.84 only selected polymers are luminescent ($\Phi_f = 0.06$) and display moderate Stokes shifts and positive emission solvatochromism.

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Introduction

In recent years the venerable electron-rich phenothiazine heterocycles have stimulated increasing scientific interest and have been successfully established in organic electronics, such as organic light-emitting diodes (OLEDs), organic field-effect transistors (OFETs), dye-sensitized solar cells (DSSCs), molecular wires and organic hole-transport layers.^{1–3} Due to their low reversible oxidation potential they qualify as good donor molecules, and butterfly shaped phenothiazines can be easily oxidized to give stable planar colorful radical cations.⁴ The optical and electrochemical properties of phenothiazines can be tuned by introducing substituents in 3- and 7-position using cross-coupling reactions, such as Suzuki and Sonogashira coupling.^{5–7} As previously shown by our group, the first oxidation potentials of phenothiazines can be lowered using mono-disperse oligophenothiazines that are accessible *via* one-pot bromine–lithium exchange–borylation–Suzuki (BLEBS) coupling.⁸ Cyclic voltammetry revealed an electronic intramolecular communication between the phenothiazine units, which can be affected by integration of covalently bound organometallic communicators, such as ferrocene.⁹ The self-assembly characteristics of oligophenothiazines bearing thioacetate groups were successfully achieved by chemisorbing the moieties on gold surfaces.^{10,11} However, solubility issues

impeded the applicability of early generations of oligophenothiazines.^{12,13}

Therefore, we became mesmerized to generate a novel conjugated organic polymer, uniting the interesting semi-conductivity of polyacetylene with the light emission of the electron-rich heterocycle of phenothiazine. Among the conjugated polymers especially the archetypal polyacetylene and novel generations of mono- and disubstituted polyacetylenes received scientific interest, showing broad applications as devices in, for instance, xerography and photovoltaic cells.^{14–17}

Very recently, we synthesized and characterized a series of novel emissive phenothiazinyl merocyanine substituted polyacetylenes accessible *via* rhodium catalysis following Taniuchi's protocol.^{18,19} Indeed, the photonic properties of phenothiazinyl merocyanines are transferable into the corresponding polymers. As monosubstituted polyacetylenes are typically regarded to be non-emissive due to unfavorable energetics of ground and excited states these results were quite surprising.²⁰ In addition, well-known solubility issues of polyacetylenes could be overcome by introducing a branched aliphatic chain.

Here, we focus on the synthesis of (oligo)phenothiazinyl substituted polyacetylenes bearing electron withdrawing and donating groups with different ligation patterns for investigating the structure–property relationships.

Results and discussion

Monomer synthesis and polymerization

The synthesis of an asymmetric alkynylated phenothiazine dimer and trimer was started with a one-pot BLEBS sequence of the mono brominated **1a** and dibrominated phenothiazine **1b**

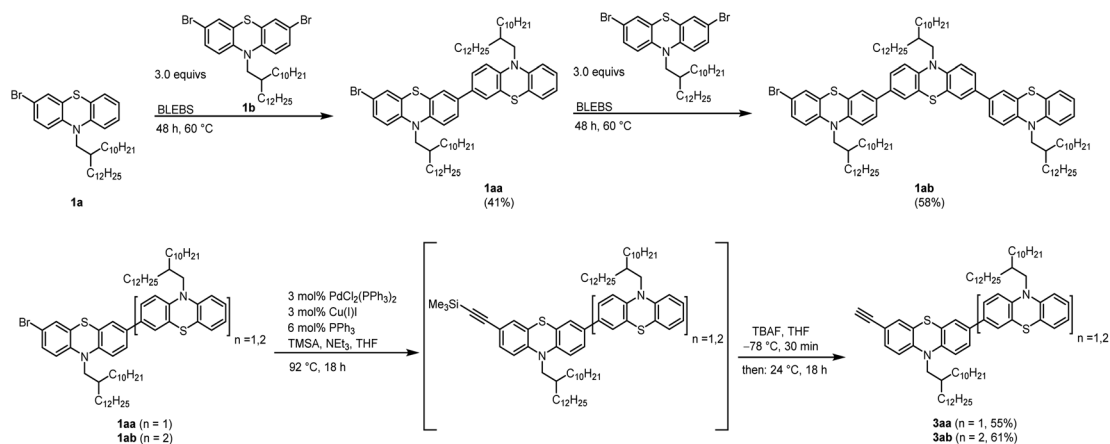
Heinrich Heine University Düsseldorf, Faculty of Mathematics and Natural Sciences, Institute of Organic Chemistry and Macromolecular Chemistry, Universitätsstrasse 1, D-40225 Düsseldorf, Germany. E-mail: Thomas.J.J.Mueller@uni-duesseldorf.de

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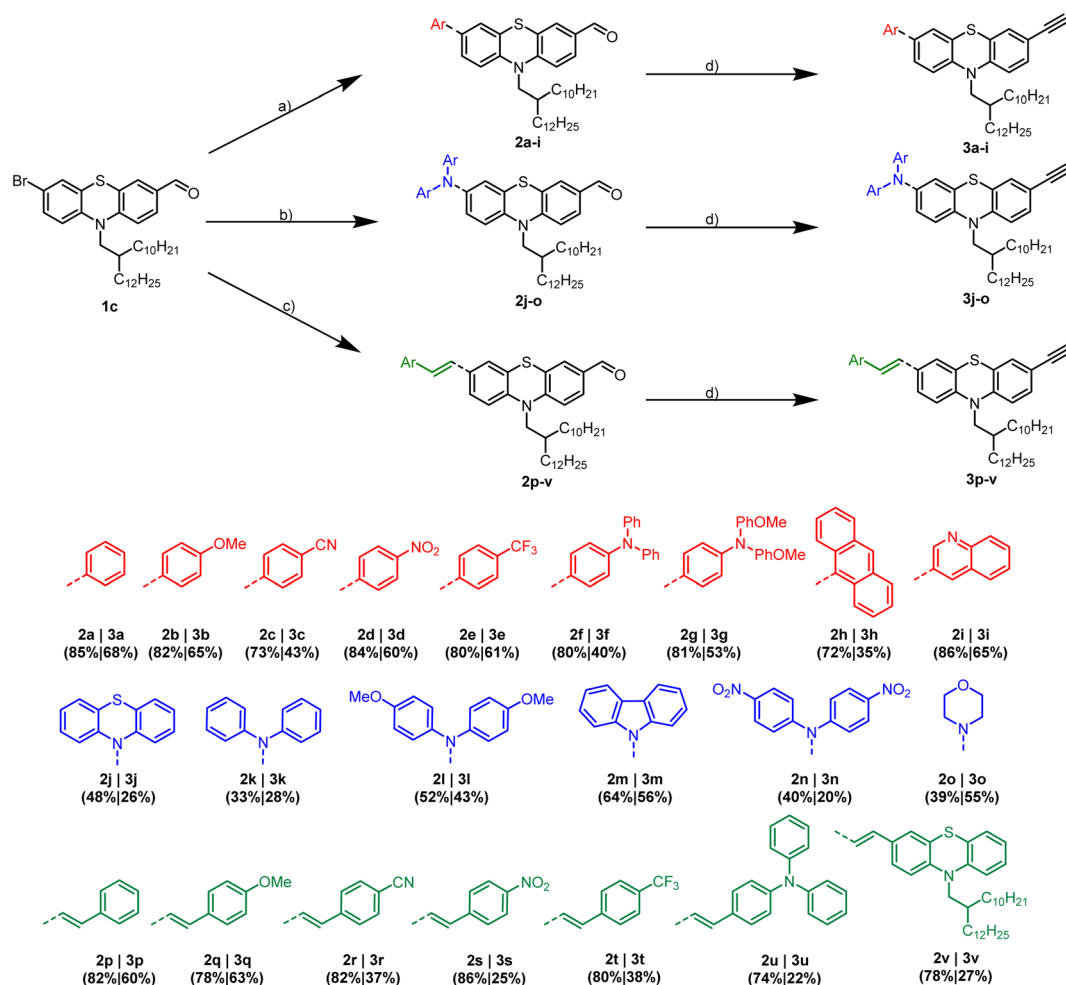


moieties according to our established protocol.⁸ In order to overcome well-known solubility issues, a branched alkyl substituent was introduced by *N*-alkylation of the phenothiazine

moiety.¹² The dibrominated phenothiazine **1b** was used in excess to minimize the formation of unfavorable symmetrical oligophenothiazines *via* double BLEBS sequence (Scheme 1).



Scheme 1 Synthesis of unsymmetrical oligophenothiazines **1aa**–**1ab** via BLEBS sequence and following synthesis of alkynylated oligophenothiazines **3aa**–**3ab** by Sonogashira-coupling-desilylation-sequence.



Scheme 2 Synthesis of 3-substituted phenothiazinyl aldehydes **2a**–**2v**. (a) Pd(PPh₃)₄, K₂CO₃, DME/H₂O, 115 °C, 16 h; (b) Pd(dba)₂, NaO^tBu, [(t-Bu)₃PH]BF₄, 1,4-dioxane, 110 °C, 18–48 h; or: Cu powder, 18-crown-6, K₂CO₃, *o*-DCB, 180 °C, 48 h; (c) Pd₂(dba)₃, NaHCO₃, cataCXium PtB, DMF, 140 °C, 16 h and of alkynylated phenothiazines **3a**–**3v** (d) Bestmann–Ohira reagent, K₂CO₃, MeOH, THF, room temp, 16 h.



The unsymmetrical brominated phenothiazines **1aa** and **1ab** were transferred into the corresponding alkynylated moieties **3aa** and **3ab** in a one-pot fashion by Sonogashira-coupling-desilylation-sequence using (trimethylsilyl)acetylene (TMSA) as a coupling reagent and tetrabutylammonium fluoride (TBAF) to deprotect the TMS group.¹⁹

The preparation of 3-substituted alkynylated phenothiazines **3** commences from bifunctional 3-bromo-7-formyl phenothiazine **1c** as starting material (Scheme 2). As recently published, **1c** is readily accessible by *N*-alkylation of 10*H*-phenothiazine with a branched swallowtail, followed by two-step Vilsmeier formylation–bromination.²⁰ Since cross-coupling reactions are a convenient method to generate libraries of substituted phenothiazines with various ligation patterns, we exploit the reactivity of phenothiazines and introduce substituents in 3- and 7-positions of the phenothiazine unit.

In the first step, electron donating and withdrawing aryl-substituents are introduced *via* Suzuki coupling using Pd(PPh₃)₄ and K₂CO₃ following our protocol⁵ to give arylated products **2a–i** in good yields (71–82%).

The donor strength of the substituents can be increased by coupling of secondary amines *via* Buchwald–Hartwig arylamination of **1c**.²¹ The corresponding phenothiazines **2j–o** are obtained in moderate yields (33–64%). Selective secondary amines are synthesized *via* Ullmann coupling since Buchwald–Hartwig arylamination is unsuccessful. Especially, electron-poor secondary amines are quite unreactive (see ESI†). Regarding the morpholino substituted derivative **2o**, an *L*-proline catalyzed variation of Ullmann coupling is required to obtain the desired product.

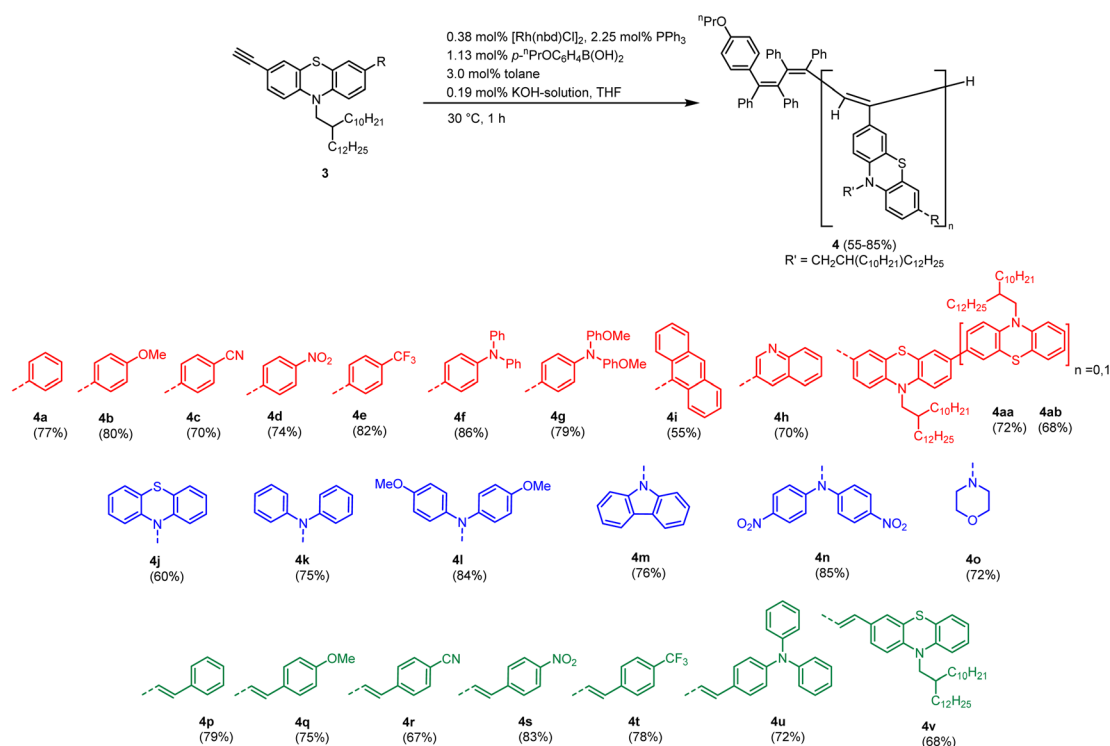
Furthermore, the π -system of the phenothiazine moieties can be extended by Heck coupling of substituted styrenes with **1c** in the presence of Pd₂dba₃ and cataCXium® PtB as a ligand.⁷ The vinylated compounds **2p–v** are isolated in good yields (74–82%). Finally, Bestmann–Ohira reaction of **2a–v** furnishes alkynylated phenothiazines **3a–v** in moderate yields, following mild conditions using a methanol–water mixture as a solvent at room temperature.⁶

The structures of the novel aldehydes **2a–v** and monomers **3a–v** are unambiguously characterized by ¹H and ¹³C NMR, IR spectroscopy and mass spectrometry. The purity of the bulk material is supported by combustion analysis.

The polymerization of the substituted alkynylated phenothiazines **3a–v** and **3aa–3ab** is accomplished following the recently optimized protocol by Taniguchi *via* rhodium catalysis (Scheme 3).¹⁸ In contrast to monomers, which are isolated as colorful oils, the corresponding polymers are precipitated in methanol furnishing orange solids. Interestingly, the obtained polymers **4** show different morphologies, including rubbers, powders, and brittle glasses.

The novel polymers **4** are characterized using gel permeation chromatography (GPC), IR spectroscopy, UV-vis absorption and emission spectroscopy. As already observed for parent polyacetylenes, NMR spectra reveal considerably broadened signals hampering a proper structural characterization.¹⁹

The solubility-promoting 2-decyl-tetradecyl *N*-substituent on the phenothiazine allows for characterization of all polymers except for anthracenyl substituted polymer **4i**, which is completely insoluble. The polymerization data are investigated using GPC measurements.



Scheme 3 Synthesis of phenothiazinyl-substituted polymers **4** by rhodium-catalyzed polymerization of 3-alkynyl phenothiazines.



Table 1 Molecular weight distributions of the polymers **4** and of corresponding unsubstituted pendant **4w** (R = H) determined from GPC traces (in THF, flow rate 1 mL min⁻¹, T = 293 K)

Polymer	M_w [kDa]	M_n [kDa]	D_M	Polymer	M_w [kDa]	M_n [kDa]	D_M
4a	205	188	1.11	4l	25.9	23.8	1.09
4b	106	103	1.06	4m	9.82	9.28	1.08
4c	138	133	1.04	4n	92.3	70.2	1.31
4d	1227	859	1.43	4o	34.9	32.7	1.06
4e	140	135	1.04	4p	68.2	66.2	1.03
4f	311	294	1.05	4q	300	156	1.92
4g	107	103	1.06	4r	392	201	1.95
4h	285	263	1.08	4s	187	11.8	15.8
4i	—	—	—	4t	93.2	90.0	1.03
4aa	107	97.1	1.11	4u	109	85.5	1.28
4ab	76.2	67.1	1.19	4v	57.7	57.8	1.01
4j	18.8	17.6	1.06	4w ¹⁹	60.0	55.8	1.05
4k	12.3	11.2	1.13				

As already observed for parent polymers, the polydispersities of phenothiazinyl substituted polyacetylenes are strongly dependent on the substitution pattern at position 7 of the phenothiazine moiety. Additionally, GPC data reveal an additional dependence on the ligation pattern. In contrast to recently published phenothiazinyl merocyanine substituted polyacetylenes,¹⁹ the obtained polymers generally show narrow weight distributions, despite applying same reaction conditions. On the one hand, aryl-substituted polymers **4a–h** and amino-substituted polymers **4j–o** show low dispersities (1.04–1.13) and high molecular weights, hinting at the living nature of this rhodium catalyzed polymerization (Table 1). On the other hand, vinyl substituted polymers **4p–4v** show wider spread of molecular weights and broad dispersities. Noteworthy, nitro substituted derivatives **4d**, **4n** and **4s** display significantly broader molecular weight distributions and lower molecular weights, which might be rationalized by interchain charge-transfer interactions of the electron-rich phenothiazinyl moieties with electron-deficient nitrostyryl parts.

An additional trend can be observed regarding the oligo-phenothiazine polymers **4aa–4ab**. In this case, longer side-chains clearly lead to broader molecular weight distributions. Comparing triad **4ab** to unsubstituted pendant **4w** (R = H),¹⁹ significantly higher polydispersities become evident indicating a low control of the polymerization (see Table 1).

Photophysical properties

The photophysical properties of monomers **3** and the corresponding polymers **4** were studied *via* UV-vis and fluorescence spectroscopy. All spectra were recorded in dichloromethane since significant emission was observed in polar solvents.

Expectedly, alkynylated phenothiazines **3** show typical photonic properties for phenothiazines. Longest wavelength absorption maxima $\lambda_{\max, \text{abs}}$ are between 334–431 nm including additional absorption bands in UV region caused by $\pi-\pi^*$ transition. Obviously, the absorption behavior is influenced by the electronic properties of the aryl substituents. A redshift of the longest wavelength absorption maxima within each series of monomers was observed for derivatives carrying electron

withdrawing substituents. Therefore, the absorption maximum of nitro-substituted derivative **3n** lies at 406 nm in contrast to donor substituted phenothiazine **3j** bearing an electron-donating phenothiazine group (328 nm). Further regularities were observed comparing aryl substituted moieties **3a–i** and corresponding vinyl substituted derivatives **3p–v**. The extension of the π -system causes a redshifted absorption from 334 to 374 nm. The same trend can be seen with phenothiazine dyad **3aa** and triad **3ab**.

Except for nitro-substituted derivatives, monomers **3** display a pronounced emission in dichloromethane. The emission maxima lie between 466 and 570 nm. Again, the strongest redshift in emission is recorded for the vinylated acceptor substituted derivative **3r**. Within the series, highest fluorescence quantum yields are detected for **3c** (0.76), **3e** (0.69), **3r** (0.87) and **3t** (0.84), bearing electron withdrawing cyano and trifluoromethyl substituents.

The optical properties of monomers **3** can be compared to the corresponding polymers **4**. Generally, the absorption and emission spectra of all monomers and polymers show a similar shape. However, for the polymers **4** additional bands are observed at 500 nm, caused by the absorption of the polyene

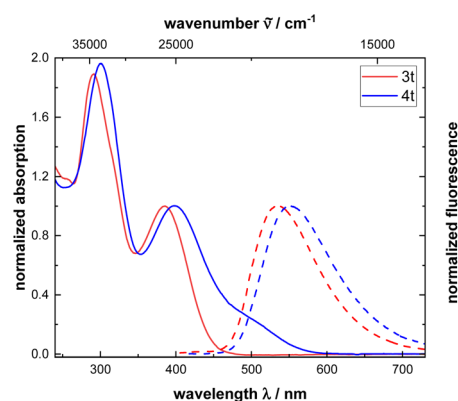


Fig. 1 UV-vis absorption and emission spectra of monomer **3t** and polymer **4t** recorded in dichloromethane ($c(\mathbf{3t}, \mathbf{4t}) = 10^{-5}$ M, T = 293 K).



Table 2 Photophysical data of monomer **3t** and polymer **4t** recorded in dichloromethane ($c(\mathbf{3t}, \mathbf{4t}) = 10^{-5}$ M, $T = 293$ K)

	$\lambda_{\max, \text{abs}}$ [nm] (ϵ [L mol ⁻¹ cm ⁻¹])	$\lambda_{\max, \text{em}}$ [nm]	Φ_{F}	Stokes shift $\Delta\tilde{\nu}^a$ [cm ⁻¹]
3t	385 (18 600), 292 (35 500)	535	0.84	7300
4t	500 (7 041 500), 399 (29 152 800), 301 (56 996 000)	551	0.06	6900

$$^a \Delta\tilde{\nu} = 1/\lambda_{\max, \text{abs}} - 1/\lambda_{\max, \text{em}} [\text{cm}^{-1}].$$

backbone. Noteworthy, the band appears as a broad shoulder. The remaining absorption maxima of polymers **4** coincide with the corresponding monomers since optical properties are determined by the phenothiazine moiety. A juxtaposition of monomer **3t** and polymer **4t** shows a redshifted absorption and emission. In contrast to alkynylated phenothiazines **3** and phenothiazinyl merocyanine substituted polyacetylenes (Fig. 1 and Table 2),¹⁹ polymers **4** are mostly weakly emissive (see ESI, Table S9†). Emission spectra are recorded, but the quantum yields are not determined since emission is very weak. Noteworthy, to measure the emission spectra of the polymers **4**, excitation is not achieved at the longest wavelength absorption band (shoulder at around 500 nm), as usually, but at the next hypsochromically shifted maximum.

Exceptionally polymers **4r** and **4t** show a moderate emission in dichloromethane with fluorescence quantum yields of 0.06, however quantum yields are significantly lower than

corresponding monomers. Moreover, both polymers exhibit pronounced polarity effects including positive emission solvatochromism (see Fig. 2 and Table 3). The lower fluorescence quantum yield in comparison to phenothiazinyl merocyanine substituted polyacetylenes¹⁹ and the lower energy of the longest wavelength absorption maxima of these series indicate that the sidechain chromophore only contributes to an emission of the polymer, if the excitation energy stems from the appended fluorophore moieties.

Conclusion

In summary, we have successfully extended the recently published library of novel soluble phenothiazinyl substituted polyacetylenes obtained *via* rhodium catalysis and analyzed their structure–property relationship. Three series of substituted alkynyl phenothiazines bearing electron withdrawing and donating substituents with different ligation patterns were synthesized applying Suzuki coupling, Buchwald–Hartwig arylation, Heck coupling and Bestmann–Ohira reaction. In contrast to parent polyacetylenes, most obtained polymers display narrow molecular weight distributions and low dispersities supporting living nature of polymerization. The photophysical properties of obtained alkynylated phenothiazines were compared to corresponding polymers. Contrary to highly emissive monomers, especially donor substituted polyacetylenes can be regarded as non-emissive. Among the series, only two polymers show moderate emission in dichloromethane (0.06), including emission solvatochromism.

Conflicts of interest

There are no conflicts to declare.

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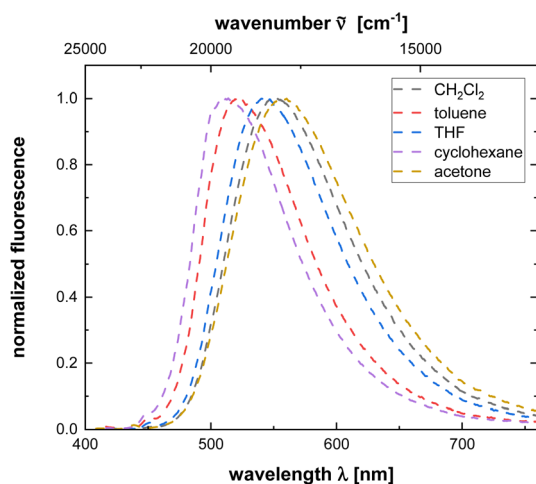


Fig. 2 Emission spectra of polymer **4t** recorded in solvents of different polarity ($c(\mathbf{4t}) = 10^{-5}$ M, $T = 293$ K).

Table 3 Photophysical data of polymer **4t** recorded in solvents of different polarity ($c(\mathbf{4t}) = 10^{-5}$ M, $T = 293$ K)

Solvent	$\lambda_{\max, \text{em}}$ [nm]	Stokes shift $\Delta\tilde{\nu}$ [cm ⁻¹]
Cyclohexane	514	5800
Toluene	522	6000
THF	543	6700
Dichloromethane	551	6900
Acetone	558	7700



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