

Synthesis of highly phenylene substituted *p*-phenylene oligomers from pyrylium salts†‡

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A transition metal free route to phenyl substituted oligophenylenes that tolerates halogens is described.

π -Conjugated oligomers and polymers are of considerable interest for chemists, physicists and materials scientists, because of their promising optical and electronic properties.¹ Moreover, their rigidity makes them attractive building blocks for molecular composite materials.² For example, poly-*p*-phenylenes (PPPs) and oligo-*p*-phenylenes (OPPs) find versatile applications as electronic conductors³ and light emitting diodes (LEDs)⁴ as well as channel-forming molecules.⁵ Mono-disperse oligomers are also important model compounds for establishing structure–property relationships in the appropriate long-chain conjugated polymers.⁶ Since unsubstituted PPPs are hardly processible, side chains need to be attached in order to process them from solution.⁷

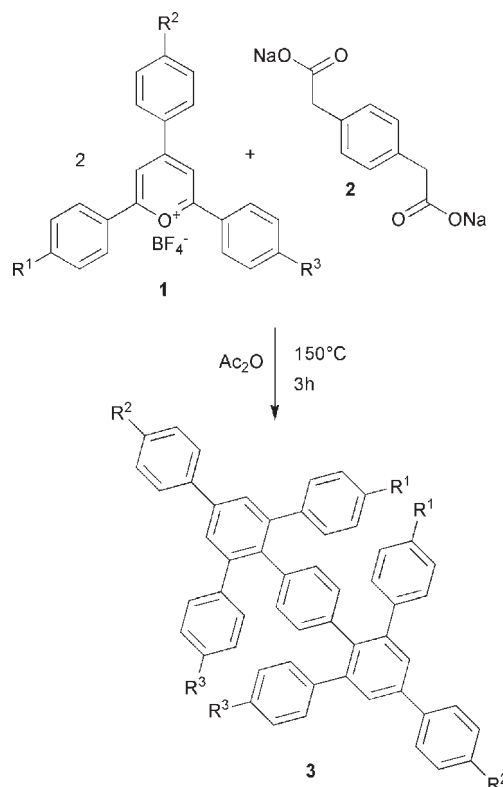
Generally, PPPs and OPPs are synthesized by metal-catalyzed cross coupling reactions of the corresponding aryl metal compound and an aryl halide.⁸ Despite considerable progress in catalyst design, coupling of sterically demanding reaction partners is still challenging.⁹ Moreover, the formation of coupling products containing aryl halide groups requires excess strategies or the intermediate introduction of protective groups.

Among alternative methods for the preparation of aryl substituted aromatics,¹⁰ condensation reactions of triarylpyrylium salts with sodium phenylacetate to 1,2,3,5-tetraarylbenzenes¹¹ offer several advantages. Triarylpyrylium salts as well as sodium arylacetates are either commercially available or easily accessible with a wide variety of substituents. The former can contain up to three different functionalized aryl groups thus giving rise to products with complex substitution patterns, even with halogen atoms. This makes their reaction

products attractive substrates for metal catalyzed coupling reactions.^{12,13}

However, we are not aware of any report about the condensation of pyrylium salts **1** with sodium 1,4-phenylenediacetate **2** to functionalized oligophenylenes **3** (Scheme 1). The reaction is carried out by heating 2.2 equivalents of **1** and 1 equivalent of **2** in acetic anhydride to reflux for 3 h. Yields are substrate dependent and vary between 2.4 and 13.4% after purification (Table 1).¹⁴

The most dominant side reaction is the formation of 1,3,5-triarylbenzenes by reaction of **1** with the solvent. Attempts to increase the yield by longer reaction times, by addition of **2** (0.5 equivalents) after 3 h and by conducting the reaction under microwave irradiation were not successful. Nevertheless, all compounds were easily isolated by column chromatography and subsequent recrystallization. The compounds were characterized by ¹H NMR, ¹³C NMR and MS.



Scheme 1 Condensation of pyrylium salt with sodium 1,4-phenylenediacetate in acetic anhydride.

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Table 1 Synthesized oligo-*p*-phenylenes

Product	R ¹	R ²	R ³	Yield (%)
3a	I	<i>t</i> -Bu	I	13.4
3b	OMe	Br	OMe	9.8
3c	I	Me	OMe	10.0
3d	<i>t</i> -Bu	Me	OMe	2.4
3e	Me	<i>t</i> -Bu	OMe	5.1
3f	<i>t</i> -Bu	<i>t</i> -Bu	OMe	6.1
3g	OMe	4-Bromophenyl	OMe	6.9

In addition, **3b** could be crystallized from dichloromethane (Fig. 1).[¶]

3b crystallizes in the monoclinic crystal system, where the molecule is located on a center of symmetry. Owing to the steric hindrance, the oligophenylene chain is not planar. Rather, the substituted phenyl ring makes an angle of 57.1° and 40.1° with the central and terminal rings, respectively. Notably, the ORTEP plot reveals fairly small thermal anisotropies reflecting a stiff arrangement. From various discotic or dendritic systems, however, it is well-known that different segments in the molecule might exhibit large differences in the mobility.^{15,16}

Molecular reorientations (*e.g.* phenyl flips) possibly occurring within the sample are conveniently probed by ²H NMR spectroscopy. Therefore, we selectively deuterated the central phenyl ring of compound **3b** (**3b-d⁴**) and performed temperature-dependent ²H NMR experiments. The ²H quadrupolar splitting that is commonly observed in the case of rigid aromatic C–D bonds is of the order of 128 kHz, while a reduction in the splitting is observed in the event of more or less defined rotational motions characterized by a dynamic order parameter.¹⁷ In the case of **3b-d⁴**, however, no motion of the core phenyl ring could be detected, and, correspondingly,

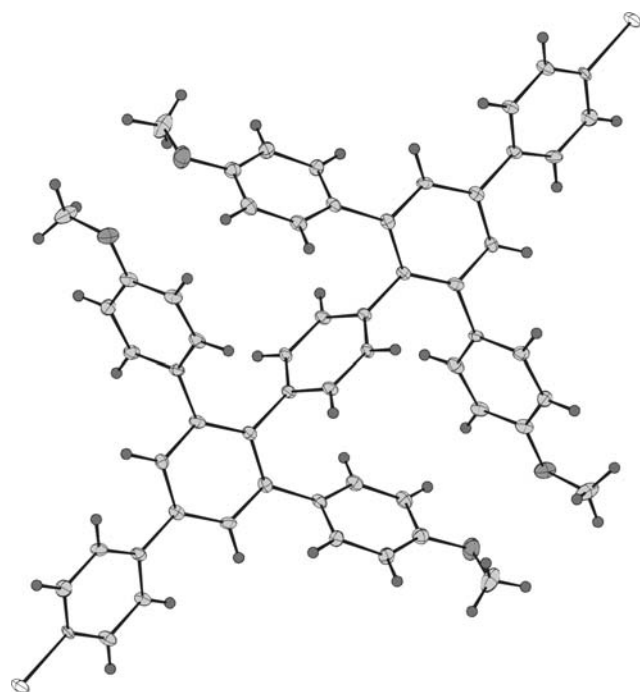


Fig. 1 ORTEP plot of the crystal structure of **3b**, thermal ellipsoids are presented at a 50% probability level.

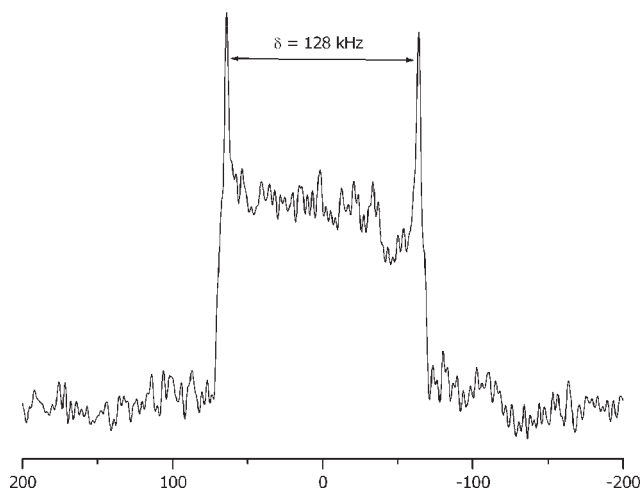


Fig. 2 ²H NMR spectrum of **3b-d⁴**.

the ²H spectrum of **3b-d⁴** has a Pake pattern with a quadrupole splitting of 128 kHz (Fig. 2). This also holds for elevated temperatures ($\approx 60^\circ\text{C}$) indicating that the core is immobile on the fast time scale ($< 10^{-4}$ s).

Although yields are at present limited, all products described here are accessible in a synthetically useful scale since pyrylium salts are easily available in large quantities. Moreover, functional group tolerance of this approach allows the introduction of halogens. These compounds are not obtainable by transition metal chemistry, unless sophisticated protecting group chemistry is used. As described before, unsymmetrical pyrylium salts ($R^1 \neq R^3$) in principle lead to the formation of two atropisomers, if one or both substituents (R^1 and/or R^3) are bulky enough to hinder free rotation of the system along its main axis. These substances and their derivatives are currently under investigation as well as optimizing the reaction conditions to obtain higher product yields.

Notes and references

¶ Preparation of **1b** ($R^1 = R^3 = \text{OMe}$, $R^2 = \text{Br}$): under an argon atmosphere, $\text{BF}_3 \cdot \text{OEt}_2$ (15 mL, 15 mmol) was added to a mixture of 1,5-bis(4-methoxyphenyl)-3-(4-bromophenyl)pentane-1,5-dione (5.0 g, 10.7 mmol) and chalcone (2.23 g, 10.7 mmol) without the use of further solvent. The mixture was stirred at 100°C for 2 h. After cooling to room temperature, diethyl ether (30 mL) was added and the red suspension was stirred for 12 h. The red precipitate was filtered off, washed with cold diethyl ether and dried in vacuum to obtain **1b** as a red powder (4.4 g, 77%). δ_{H} (400 MHz, DMSO-d_6) 8.80 (s, 2 H), 8.46 (d, J 9.01, 4 H), 8.41 (d, J 8.75, 2 H), 7.93 (d, J 8.69, 2 H), 7.25 (d, J 9.05, 4 H), 3.95 (s, 6 H); δ_{C} (400 MHz, DMSO-d_6) 170.0, 165.8, 162.8, 133.6, 132.8, 132.3, 132.0, 130.0, 122.3, 116.4, 113.5, 57.0.

Preparation of **3b**: a mixture of **1b** ($R^1 = R^3 = \text{OMe}$, $R^2 = \text{Br}$) (15.1 g, 28.2 mmol), **2** (3.02 g, 12.8 mmol) and Ac_2O (125 mL) was stirred at 150°C for 3 h. After cooling to room temperature, Ac_2O was removed in vacuum and the residue was digested in dichloromethane and filtered over a short column of silica gel with dichloromethane as eluent. The final purification was carried out by column chromatography using dichloromethane–petroleum ether (1 : 1) ($R_f = 0.45$ in dichloromethane–petroleum ether 1 : 1) and subsequent precipitation from dichloromethane by the addition of petroleum ether. **3b** (660 mg, 9.8%) was obtained as a white solid. NMR: δ_{H} (500 MHz, CD_2Cl_2) 6.57 (s, 8 H), 7.53 (s, 4 H), 6.98 (d, J 8.81, 8 H), 6.74 (d, J 8.81, 8 H), 6.57 (s, 4 H), 3.78 (s, 12 H); δ_{C} (500 MHz, CD_2Cl_2) 158.4, 142.2, 139.5, 138.5, 137.9, 136.9, 134.3, 131.9, 131.1, 131.0, 128.7, 128.0, 121.6,

113.0, 55.2; UV (CH₂Cl₂): λ_{max} = 260.5 nm; fluorescence (CH₂Cl₂): λ = 388 nm; MS (FAB): m/z = 964.3; mp: 299–302 °C

¶ Crystallographic data for **3b**: C₅₈H₄₄Br₂O₄, M = 964.79, monoclinic, a = 9.3964(5), b = 9.7344(5), c = 23.5694(8) Å, α = 90, β = 91.8388(12), γ = 90°, V = 2154.7(2) Å³, T = 120 K, space group $P2_1/n$, Z = 2, 25 844 reflections measured, 5840 unique (R_{int} = 0.0439), $R1$ = 0.0439. The final $wR(F_2)$ was 0.0468 (all data). CCDC 686812.

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