Tetrahedron 64 (2008) 11475–11479

Contents lists available at ScienceDirect

Tetrahedron

journal homepage: www.elsevier.com/locate/tet

Upon the intrinsic optical properties of oligo(*p*-phenyleneethynylene)s (OPEs). Synthesis of OPE3 for experimental gas-phase absorption studies

Torben Ryhding [a], Maj-Britt Suhr Kirketerp [b], Umesh Kadhane [b], Morten Køcks Lykkegaard [b], Subhasis Panja [b], Steen Brøndsted Nielsen [b,*], Mogens Brøndsted Nielsen [a,*]

[a] *Department of Chemistry, University of Copenhagen, Universitetsparken 5, DK-2100 Copenhagen Ø, Denmark*
[b] *Department of Physics and Astronomy, University of Aarhus, Ny Munkegade, DK-8000 Aarhus C, Denmark*

ARTICLE INFO

Article history:
Received 5 June 2008
Accepted 20 August 2008
Available online 27 August 2008

Keywords:
Cross-coupling
Electrostatic interactions
Ionization energy
OPE
Spectroscopy

ABSTRACT

A new oligo(*p*-phenyleneethynylene) (OPE3) was synthesized by step-wise Pd-catalyzed cross-coupling reactions. The molecule incorporates an amine functionality, which allows for transfer of the protonated molecule to the gas phase by electrospray ionization leaving the OPE entity neutral. This method has allowed for the first experimental gas-phase absorption spectrum of an OPE3 by action spectroscopy, employing an electrostatic ion storage ring in combination with a laser system. The studies reveal the effect of having a positive charge in proximity to the conjugated backbone of OPE3 in the absence of any interfering solvent molecules. In addition, ionization energies and electron affinities of OPE2–OPE17 were calculated at the density functional theory (DFT) level.

1. Introduction

Conjugated polymers have found wide applications in materials chemistry as laser dyes, light-emitting diodes, organic conductors, photoconductors and nonlinear optical (NLO) materials.[1] Their materials' properties are to a large extent determined by the optical band gap. The poly(*p*-phenyleneethynylene)s (PPEs) represent one type of conjugated polymers that by suitable functionalization can be employed, for example, for explosive detection or polarizers for LC displays.[2] In the conjugated oligomer approach,[3] the optical properties of a series of monodisperse oligomers are investigated and then extrapolated to ideal infinite polymers. These conjugated oligomers are interesting in their own right, for example, as molecular wires for molecular electronics.[4]

One challenge is to make meaningful comparisons between experimental excitation energies obtained in solution or in the solid state and those calculated by quantum chemical means on isolated molecules. Intermolecular or molecule–solvent interactions as well as solid-state packing effects may perturb the electronic structure and cause a shift in the transition energy. This problem calls for studies on isolated molecules in the gas phase, free of a disturbing environment. However, often the macromolecules are too fragile to be evaporated for gas-phase absorption spectroscopy. Instead charged chromophores can often be brought in the gas phase by electrospray ionization (ESI) and their absorption can then be measured by sophisticated action spectroscopy techniques, that is, absorption is monitored by a detection of ionic fragmentation. In Aarhus, we use the electrostatic ion storage ring, ELISA,[5] as a gas-phase optical cell for such measurements. As an example, several biochromophores have been investigated using this approach, shedding light on absorption tuning by protein interactions.[6]

For investigating neutral chromophores by this method, we need to attach a charged group, a so-called spectator charge, to allow for electrospray ionization. Otherwise the chromophore itself would become charged under the conditions. This spectator charge should be placed at a remote position if the goal is to reveal the intrinsic properties of the neutral chromophore; i.e., the spectator charge should for this purpose be placed at a position at which it does not interfere with the chromophore. On the other hand, the method also allows us to investigate systematically the influence of approaching a positive or negative charge to the chromophore. We became interested to explore the properties of oligo(*p*-phenyleneethynylene)s (OPEs, Fig. 1) and present here the synthesis of an OPE3 incorporating an amino group as protonation site. The first experimental gas-phase absorption spectrum was recorded of this OPE under the influence of a positive ammonium group as spectator charge. The result of this nontrivial experiment can be compared directly with quantum chemical calculations. In addition, the

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* Corresponding authors.
E-mail addresses: sbn@phys.au.dk (S.B. Nielsen), mbn@kiku.dk (M.B. Nielsen).

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doi:10.1016/j.tet.2008.08.068

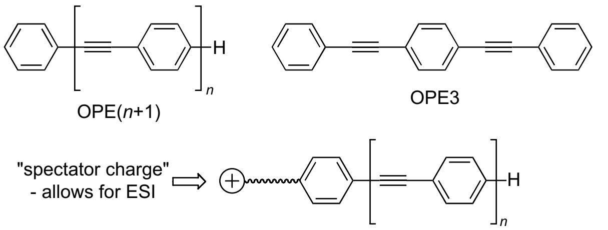


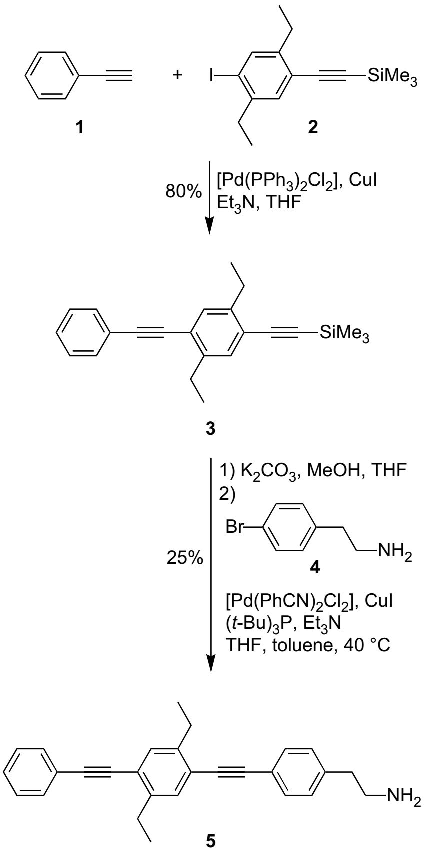
Figure 1. Oligo(*p*-phenyleneethynylene)s (OPEs). To allow for electrospray ionization (ESI), a charged group is attached, a so-called spectator charge.

intrinsic properties of OPEs were investigated in a computational study of ionization energies and electron affinities.

2. Results and discussion

2.1. Synthesis

The synthesis of the OPE3 model compound is shown in Scheme 1. We chose to attach an amine functionality, being precursor for an ammonium spectator ion, by an ethyl linker to the chromophore. First, a Sonogashira cross-coupling reaction[7] between phenylacetylene **1** and aryl iodide **2**[8] gave compound **3**. This compound was desilylated using K_2CO_3 in MeOH/THF, and the resulting terminal alkyne was then subjected to a cross-coupling reaction with the aryl bromide **4** to furnish the OPE3 **5**. Here the catalyst conditions for coupling of aryl bromides developed by Hundertmark et al.[9] were employed. These conditions allowed coupling of the aryl bromide **4** at 40 °C. The product **5** exhibited limited solubility, but it was soluble enough to allow for the gas-phase spectroscopic studies aimed at.



Scheme 1.

2.2. Gas-phase action spectroscopy

Gas-phase experiments on the OPE3 **5** were carried out at the ELectrostatic Ion Storage ring in Aarhus (ELISA). The experimental setup is shown in Figure 2 and has been described in detail elsewhere.[5,6] Electrospray ionization of **5** dissolved in water and methanol (1:1) with 5% acetic acid added produced the bare $\mathbf{5}\cdot H^+$ ions in the gas phase. Ions were accumulated for 0.1 s in a 22-pole ion trap in which they were thermalized from collisions with helium buffer gas. The ion bunch was accelerated to 22-keV kinetic energies, and selection of ions of interest according to their mass-to-charge ratio was then done by a bending magnet ($\mathbf{5}\cdot H^+$: m/z=378). These ions were injected into the ring and stored. The storage time in the ring was about a second, limited by collisions with residual gas at a pressure of a few times 10^{-11} mbar. Ionic dissociation in the same side as the injection side was monitored from counting the neutral particles that hit the microchannel plate detector at the end of the section. After about 35.1 ms, ions were irradiated with a 4-ns pulse of light from an EKSPLA laser that produced tunable light between 210 and 390 nm. Light absorption was monitored by an increased yield of neutrals from delayed dissociation of the photoexcited ions. A measurement of the neutrals yield divided by the number of photons in the pulse and normalized to the yield from collision induced dissociation as a function of wavelength provided the absorption spectrum.

The decay spectrum of isolated $\mathbf{5}\cdot H^+$ ions in the ring is shown in Figure 3. The revolution time of the ions in the ring is

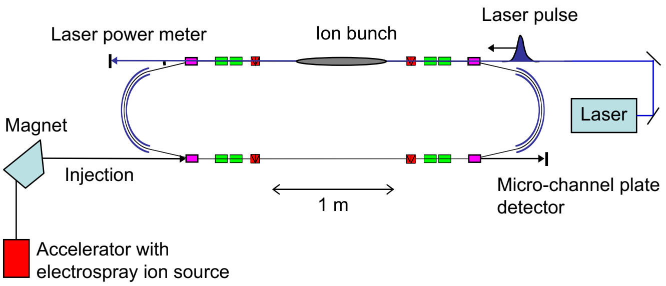


Figure 2. The electrostatic ion storage ring in Aarhus, ELISA, in combination with a laser system. The photofragment yield was measured as a function of wavelength from the signal of neutrals hitting the detector. See text for details.

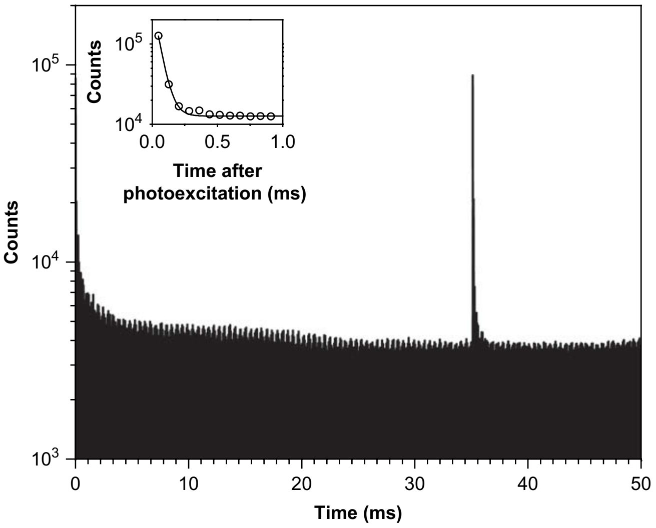


Figure 3. Decay spectrum of $\mathbf{5}\cdot H^+$ ions. After 35.1 ms of storage, the ions were photoexcited with 320-nm light. The inset shows the signal as a function of time after photoexcitation.

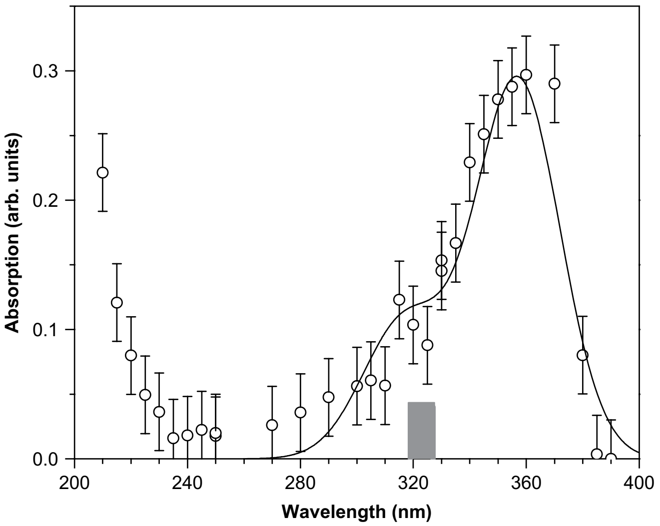
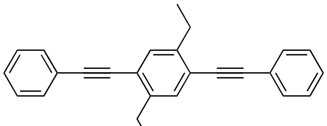


Figure 4. Absorption spectrum of $\mathbf{5}\cdot\text{H}^+$ ions isolated in vacuo. The grey box indicates the region in which λ_{max} is usually found in solution for OPE3s (see text for details).

78 µs. The high number of neutrals detected immediately after injection is due to metastable ions that have been excited during extraction from the ion trap. After a few milliseconds, the signal is dominated by collisional decay in the ring. After 35.1 ms, the ions were photoexcited with 320-nm light, which resulted in a large number of neutrals from delayed ionic dissociation. The decay is due to one-photon absorption according to a power dependence study (data not shown) and is well-described by an exponential with a time constant of 46 µs. From a separate experiment in which ring voltages were switched to store daughter ions,[10] the dominant reaction channel was found to be loss of ammonia.

In Figure 4 we present the absorption spectrum of bare $\mathbf{5}\cdot\text{H}^+$ ions. The gas-phase spectrum reveals maximum absorption at λ_{max}=357 nm, a shoulder at ca. 317 nm and an absorption band with maximum below 210 nm, the lower limit of the laser. Previous solution studies (in hexane) on the parent unsubstituted OPE3 revealed an absorption maximum at 319 nm and a shoulder at 338 nm.[11] In chloroform, absorption at 322 nm was reported and in dioxane at 320 nm.[12] For compound **6** incorporating two ethyl substituents at the central ring, a slightly redshifted absorption maximum at 327 nm in dichloromethane was reported.[13] It is noticed that the absorption band of the neutral chromophore in solution phase is in between the two bands observed for the cation in gas phase. Since a small redshift of the absorption is expected if the cation is dissolved in an apolar solvent, the difference between the absorption of the cation and neutral chromophore must be ascribed to the presence of the charged ammonium group. In other words, the ammonium group is not an innocent spectator when placed at the current position. A simple explanation of the two bands of the cation is an asymmetric charge distribution in the excited state: either the active electron is closer to the positive charge in the excited state than in the ground state or it has moved in the opposite direction, away from the charge. In the first case, we have an excited state that is stabilized more than the ground state and in the second a ground state that is stabilized more than the excited state by the presence of the charge. This model would result in one band to the blue and one to the red relative to the neutral chromophore. To test this idea, we plan in the future to place an ammonium group symmetrically at both sides of the chromophore, in which case only a single band is expected. In another approach, the spectator charge is to be placed at a more remote position in order not to interfere with the absorption properties.



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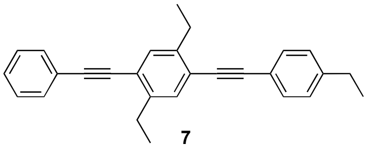

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James et al.[14] have calculated the excitation energy of the parent OPE3 and obtained a value of 360 nm using time-dependent density functional theory (TD-DFT) and a value of 365 nm at the ZINDO/S level. We also performed TD-DFT calculations (B3LYP/6-311++G*) on B3LYP/6-31G(d) geometry-optimized structures using the Gaussian 03 program package.[15] The calculated value for the neutral, parent OPE3 is 367 nm, while the ethyl-substituted OPE3s **6** and **7** exhibit slightly redshifted values of 370 and 374 nm, respectively. Despite the fact that the calculated values are close to the experimental one, they still seem to overestimate the intrinsic absorption maximum as the experimental value is influenced by the positive charge in proximity to the conjugated system.

2.3. Computational study: ionization energies and electron affinities

A selection of OPE(n)s (n=2–17) was geometry-optimized at the semi-empirical PM3 level. The structure of fully planar OPE17 is shown in Figure 5. Then, single-point energies were calculated at the B3LYP/6-311++G(2d,p) level on the neutral, radical cation and radical anion structures (using the geometries of the neutral molecules). From these data, the vertical ionization energies (IE) and vertical electron affinities (EA) were calculated and collected in Table 1. These energies are plotted as a function of the inverse total number (N) of π-electrons in Figure 6. Linear extrapolation to an infinite PPE provides an IE of 5.80 eV. Hovewer, it should be noted that the points do not follow a straight line perfectly, and this IE of an infinite polymer seems to be slightly overestimated. For comparison, an experimental IE of PPE was determined to be 6.3 eV with ultraviolet photoelectron spectroscopy and 5.8 eV with cyclic voltammetry.[16] By extrapolation of the calculated data, an EA of 2.34 eV for PPE is obtained. Deviation from a perfect straight line is

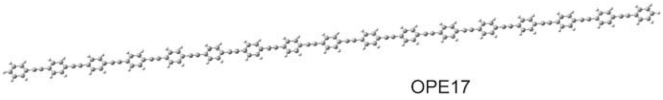

Figure 5. PM3-optimized structure of planar OPE17.

Table 1
Vertical ionization energies (IE) and electron affinities (EA) calculated at the B3LYP/6-311++G(2d,p) level on PM3 geometry-optimized neutral structures

	OPE2	OPE3	OPE4	OPE5	OPE6	OPE7	OPE8	OPE9
IE/eV	7.60	7.02	6.72	6.54	6.41	6.31	6.27	6.19
EA/eV	0.17	0.84	1.19	1.40	1.57	1.70	1.79	1.88

	OPE10	OPE11	OPE12	OPE13	OPE14	OPE15	OPE16	OPE17
IE/eV	6.15	6.14	6.05	6.03	6.01	5.94	5.93	6.01
EA/eV	1.94	1.97	2.02	2.06	2.09	2.12	2.15	2.16

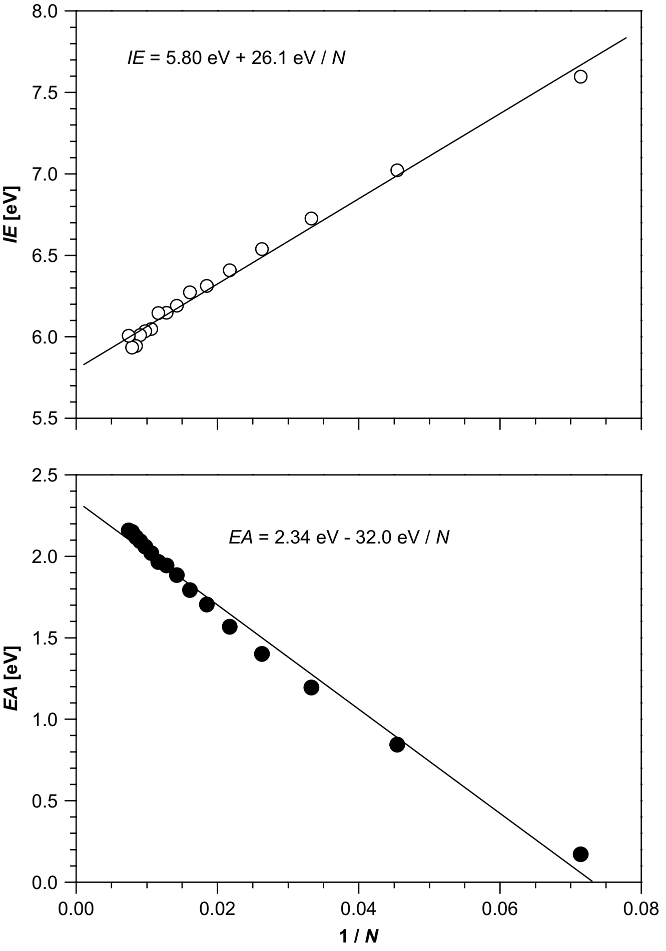

Figure 6. Ionization energies (IE) and electron affinities (EA) for OPEs as a function of the inverse number of π-electrons (*N*).

more significant here and may underestimate the EA of PPE by ca. 0.1 eV. Subtracting the linearly extrapolated IE and EA values gives a band gap of 3.46 eV for PPE. This value is the estimated band gap of an isolated, completely planar PPE. For comparison, alkyl-substituted PPEs typically exhibit a broad unresolved absorption in solution at 384/388 nm (ca. 3.2 eV), and an absorption in films at 435 nm (2.9 eV).[2,17]

3. Conclusions

An OPE3 incorporating an amino functionality was prepared by step-wise cross-coupling reactions. The amino group allows for transfer of the chromophore as the protonated species to the gas phase by electrospray ionization. Electrospray ionization in combination with the storage ring technique prevents the necessity for evaporating the molecules in order to perform gas-phase spectroscopy and we have measured the first experimental gas-phase absorption spectrum of an OPE3 ammonium cation. The major absorption maximum is found to be significantly redshifted in the gas phase as compared to solution phase, which is ascribed to the stabilizing effect of the excess charge on the diffuse $\pi\pi^*$ state. The method is by no way trivial and the optical properties of other OPE model compounds await to be investigated in future work. In addition, we have calculated vertical ionization energies and electron affinities for a large selection of OPEs and predict by extrapolation values of 5.80 and 2.34 eV, respectively, for an isolated, completely planar PPE.

4. Experimental

4.1. General experimental procedures

Dry solvents were provided by an Innovative Technology Puresolv apparatus, or dried over 4 Å molecular sieves. Merck silica gel (0.040–0.063 mm) was used for flash column chromatography. TLC was performed on silica gel coated aluminium foils (Merck alumina foil 60 F_{254}). NMR spectra were obtained using a Varian 300 MHz NMR spectrometer at room temperature. Fast Atom Bombardment (FAB) mass spectra were obtained on a Jeol JMS-HX 110 Tandem Mass Spectrometer in the positive ion mode. Electrospray ionization spectra were recorded on a ZAB-EQ (VG-Analytical) instrument. Melting points were measured on a Reichert melting point apparatus equipped with a microscope and are uncorrected. Elemental analyses were performed at Department of Chemistry, University of Copenhagen.

4.2. 1,4-Diethyl-2-(phenylethynyl)-5-(trimethylsilylethynyl)-benzene (3)

To a solution of the iodide **2** (0.51 g, 1.43 mmol), $Pd(PPh_3)_2Cl_2$ (50 mg, 0.07 mmol) and CuI (24 mg, 0.13 mmol) in THF (10 mL) were added phenylacetylene **1** (0.20 mL, 1.7 mmol) and Et_3N (2 mL). The reaction mixture was stirred for 24 h under Ar. Then, it was diluted with CH_2Cl_2 (20 mL) and washed with saturated aqueous NH_4Cl (20 mL). The organic phase was dried with $MgSO_4$, filtered and concentrated in vacuo. Purification by flash chromatography (SiO_2, *c*-hexane) gave the product as a colourless oil (0.38 g, 80%). ^1H NMR ($CDCl_3$, 300 MHz) δ=0.28 (s, 9H, CH_3), 1.27 (t, *J*=7.5 Hz, 3H, CH_3), 1.30 (t, *J*=7.4 Hz, 3H, CH_3), 2.79 (q, *J*=7.5 Hz, 2H, CH_2), 2.84 (q, *J*=7.4 Hz, 2H, CH_2), 7.36 (m, 5H, Ar), 7.54 (m, 2H, Ar). ^{13}C NMR ($CDCl_3$, 75 MHz) δ=0.23, 14.77, 14.95, 27.37, 27.40, 88.38, 94.30, 99.36, 104.07, 122.54, 122.87, 123.66, 128.53, 128.63, 131.72, 131.74, 132.07, 143.56, 144.19. MS (FAB): *m*/*z*=330 (M^+). Anal. Calcd for $C_{23}H_{26}Si$: C, 83.57; H, 7.93. Found: C, 83.51; H, 8.17.

4.3. 1-[4-(2-Aminoethyl)phenylethynyl]-2,5-diethyl-4-(phenylethynyl)benzene (5)

Compound **3** (0.121 g, 0.367 mmol) was treated with K_2CO_3 (0.20 g, 1.4 mmol) in a $MeOH/CH_2Cl_2$ mixture (1:1, 10 mL). After complete desilylation (judged by TLC, approx. 45 min), the mixture was diluted with Et_2O (20 mL) and washed with water (2×20 mL). The organic phase was dried with $MgSO_4$, filtered and concentrated in vacuo to furnish the deprotected alkyne. $Pd(PhCN)_2Cl_2$ (25 mg, 0.065 mmol) and CuI (6 mg, 0.03 mmol) were dissolved in THF (1 mL) and toluene (1 mL). Then, *i*-Pr_2NH (0.34 mL) and *t*-Bu_3P (0.25 mL, 10% in hexanes) were added to this catalyst mixture. The catalyst solution was then added to the deprotected alkyne and aryl bromide **4** (0.109 g, 0.55 mmol) under argon, and the reaction mixture was left overnight at 40 °C. The mixture was concentrated in vacuo, whereupon the residue was dissolved in warm toluene. Pentane was added to precipitate the product as a slightly yellow solid (37 mg, 25%) of limited solubility. Mp 180 °C (decomp.). ^1H NMR (DMSO-d_6, 300 MHz): δ=1.21 (m, 6H, CH_3), 2.75–3.03 (m, 8H, 4×CH_2), 7.21 (d, *J*=7.2 Hz, 2H, Ar), 7.34 (d, *J*=7.3 Hz, 2H, Ar), 7.44 (m, 2H, Ar), 7.50 (m, 3H, Ar). HRMS (ESI): *m*/*z*=378.2211 (MH^+); calcd for $C_{28}H_{28}N$: 378.2216.

Acknowledgements

This work was supported by Lundbeckfonden and Direktør Ib Henriksens Fond.

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