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Octupolar organometallic Pt(II) NCN-pincer complexes; Synthesis, electronic, photophysical, and NLO properties

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This paper is dedicated to Professor Irina P. Beletskaya in recognition of her great and innovative research in the field of metal mediated and catalyzed organic synthesis; thank you for your friendship and many inspiring discussions. Happy birthday!

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ABSTRACT

A series of organometallic octupolar 1,3,5-substituted-2,4,6-styryl-benzene complexes was synthesized by post-modification of parent [PtCl(NCN-CHO-4)], i.e. 1,3,5-tri-R-2,4,6-tris[(4-(PtCl)(3,5-bis[(dimethylamino)methyl]styryl)]benzene (NCN = [C₆H₂(CH₂NMe₂)₂-2,6][−] in which R = OMe, H, Br (**1–3**). Their synthesis involved a triple Horner-Wadsworth-Emmons reaction of [PtCl(NCN-CHO-4)] with the appropriate tris[(diethoxyphosphoryl)methyl]benzene derivative. The ¹⁹⁵Pt{¹H} NMR chemical shift reflects the electronic properties of the π-system to which it is connected. The UV/Vis bands of the octupolar platinum complexes are only slightly red-shifted (by 5–12 nm) with respect to those of corresponding stilbenoid Pt-Cl pincer compounds (i.e., the separate branches), suggesting that there is only a limited electronic interaction between these branches. The fluorescence Stokes shift, quantum yields and lifetimes of **1–3** also are of the same order of magnitude as those of stilbenoid Pt-Cl pincer compounds, indicating that a dipolar excited state is formed, which is localized on one of the three branches. The hyper-Rayleigh scattering technique revealed hyperpolarizabilities β_{HRS} of 430, 870 and 183 × 10^{−30} esu for **1**, **2** and **3**, respectively, which are among the highest for transition metal complexes. The highest value was found for the compound lacking a donor or acceptor group at the central core, lending support to the idea that dispersion overwhelms charge transfer in determining the magnitude of the first hyperpolarizability in octupolar compounds.

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1. Introduction

The development of new optical materials containing organometallic groupings attracts a great deal of attention in materials research. Materials with notable non-linear optical properties [1–6] or light-emitting diode properties [6–8] have been discovered, comprising molecules in which one or several organometallic fragments are connected to a conjugated system. The observed

optical and photophysical properties of these materials often rely also on the presence of electron donor and/or acceptor groups. Depending on the nature of these latter groupings and the conjugated system, the electronic properties and/or the nonlinear optical (NLO) properties can be fine-tuned [9,10].

Guerchais et al. reported an example of electronic fine tuning for cyclometalated Pt^{II} complexes, containing a 4-styryl-2-phenylpyridine ligand, with different substituents on the styryl group [8]. In a similar study we reported on 4,4'-disubstituted stilbenoid NCN-pincer Pt^{II} complexes [PtCl(NCN-R-4)] (NCN-R-4 = [C₆H₂(CH₂NMe₂)₂-2,6-R-4][−] in which R = C₂H₂C₆H₄-R'-4', with R' = NMe₂, OMe, SiMe₃, H, I, CN, NO₂), see Fig. 1 [11]. For these

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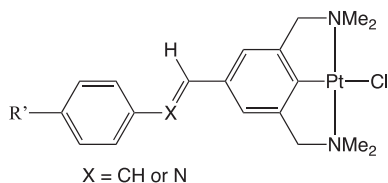


Fig. 1. Stilbenes (X = CH) and benzylideneanilines (X = N) used for studying donor-acceptor communication between *para*-R substituents and the Pt-Cl fragment [11,12].

systems a linear correlation was found between the Hammett substituent constant σ_p of R' , and the δ ^{195}Pt NMR chemical shifts of the metal center, pointing to a substantial electronic interaction of the *para* positioned substituents and the NCN-Pt^{II} fragment. Photoinduced charge separation, in which the Pt functionality functions as an electron donor, was shown to occur. The nature of the donor-acceptor interaction, i.e. in terms of separate inductive and mesomeric contributions, between the *para*-substituent and the NCN-Pt^{II} fragment could be further studied in a series of organometallic 4,4'-substituted benzylidene aniline complexes 4-ClPt-3,5-(CH₂NMe₂)₂C₆H₂CH = NC₆H₄R'-4', with $R' = \text{NMe}_2, \text{Me}, \text{H}, \text{Cl}, \text{CN}$, see Fig. 1 [12].

Linear correlations were found between the azomethine ^1H , the ^{195}Pt NMR and various ^{13}C NMR chemical shifts, and the substituent parameters σ_F and σ_R of R' at the aniline site. The dual substituent parameter treatment of the azomethine ^{13}C NMR shift gave important insight into the unique behavior of the Pt-pincer group as a substituent. Inductively, it is a very strong electron-withdrawing group, whereas mesomerically it behaves like a very strong electron donating group [12].

Within non-linear optics research, octupolar compounds represent an interesting class of materials [13–15]. In general, compounds consisting of a multi-branched conjugated backbone with three-fold (approximate D_{3h}) symmetry have been subject of investigation [16]. These compounds consist of a central core with either electron donating or accepting characteristics to which three π -conjugated branches are connected, which often also contain electron accepting or donating substituents. The relation between the NLO-characteristics and the charge transfer pattern is, however, not immediately obvious [17]. Organometallic and coordination compounds have also been explored as octupolar NLO materials [18–21].

Building on our success with the 4,4'-disubstituted stilbenoid and benzylideneaniline bridged pincer Pt-complexes, we were interested as to whether octupolar NLO-active compounds could be developed from these pincer compounds. Hence, in this study we report the synthesis and optoelectronic properties of donor/acceptor substituted octupolar stilbenoid NCN-pincer platinum complexes 1,3,5-tri-R-2,4,6-tris[(4-(PtCl)(3,5-bis[(dimethylamino)methyl]styryl)]benzene ($R = \text{OMe}, \text{H}, \text{Br}$) (**1–3**) (Fig. 2).

These molecules contain a central aromatic ring, to which three styryl NCN-pincer platinum fragments are connected on the *meta* positions. The central aromatic ring will be used to tune the electronic properties by the introduction of substituents R . The complexes are fully characterized using NMR, IR, high resolution mass spectroscopy, and with elemental analysis. Furthermore, the electronic, physical, and optical properties of these compounds are studied using NMR, UV/Vis, emission spectroscopy and hyper-Rayleigh scattering (HRS).

2. Results and discussion

2.1. Synthesis

In our (post-modification) strategy to synthesize the organometallic octupolar molecules **1–3**, we used the Horner-

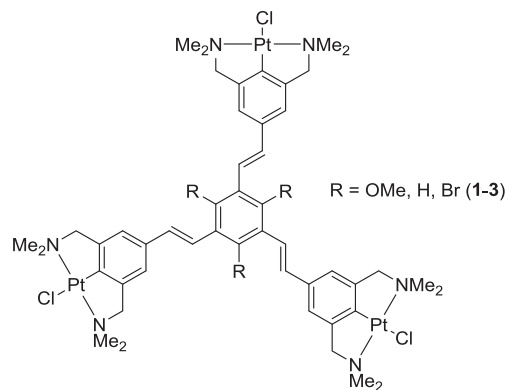


Fig. 2. Donor-acceptor star shaped stilbenoid pincers.

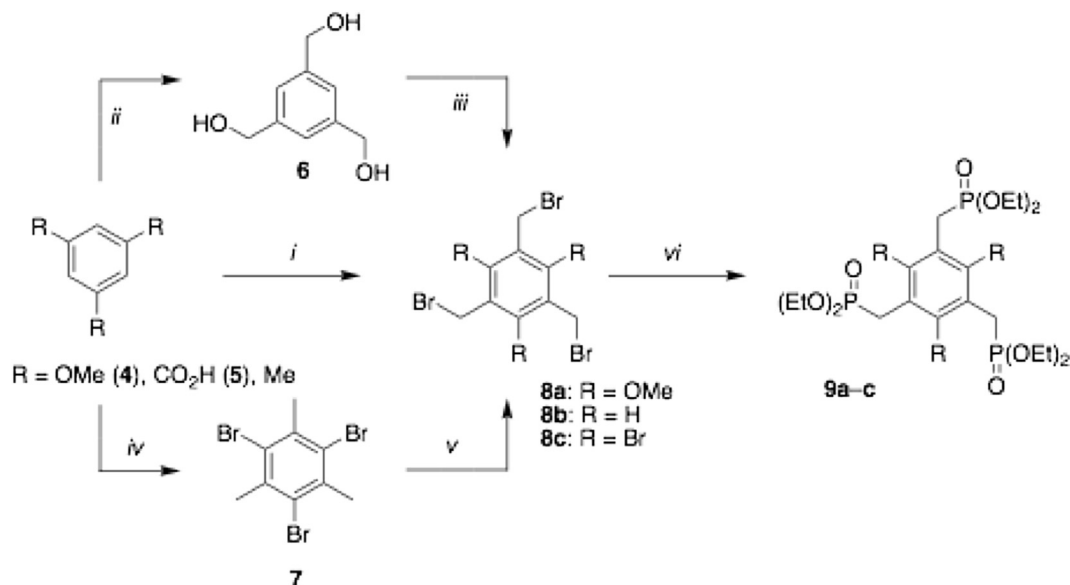
Wadsworth-Emmons protocol (see Scheme 2) [22]. In this reaction a benzylphosphonate ester is coupled with an aromatic aldehyde, in the presence of a strong base (tBuOK). After hydrolysis, the two fragments are connected via a carbon-carbon double bond, with a predominant *trans* configuration. The Horner-Wadsworth-Emmons protocol was used in the previously reported synthesis of the 4,4'-substituted stilbenoid NCN pincer Pt(II) complexes, and showed to be compatible for the organometallic pincer platinum fragment [11]. To afford a series of electronically different octupolar complexes, first the diethyl benzylphosphonate ester precursors **9a–c** had to be synthesized. This was done according to reported procedures (Scheme 1). Thus, benzyl bromide **8a** ($R = \text{OMe}$) was synthesized via bromomethylation of the aromatic ring of the commercially available 1,3,5-trimethoxybenzene **4** using formaldehyde and a mixture of HBr/acetic acid (reaction i) [13,23,24].

Benzyl bromide **8b** ($R = \text{H}$) was obtained via a multistep reaction procedure starting with 1,3,5-benzenetricarboxylic acid **5** which was converted into tris-benzylalcohol **6** (ii), which was subsequently converted into **8b** with a mixture of HBr/acetic acid (iii) [22,25]. Tribromomesitylene **7** was obtained via an aromatic bromination of mesitylene with bromine (iv) [26]. In the next step (v) **7** was converted into benzyl bromide **8c** by a radical bromination of the mesityl groups using N-bromosuccinimide [27]. Finally the benzyl bromides **8a–c** were converted into the benzylphosphonate esters **9a–c**, according a Michaelis-Arbusov reaction with triethylphosphite (*vide infra*) [13,22,28].

As described above, in order to synthesize the organometallic octupoles, metallo-aldehyde [PtCl(NCN-CHO-4)] (**10**) was coupled with the corresponding benzylphosphonate esters **9a–c**. After hydrolysis of the reaction mixture, the pure *trans* isomers of the octupoles **1–3** were isolated in good yields (75–92%), noting that this reaction involves three coupling reactions on one central molecule (Scheme 2).

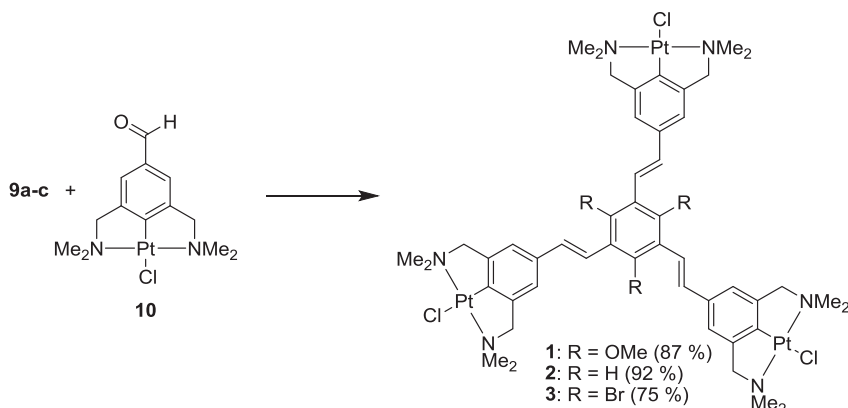
2.2. NMR spectroscopy

Solutions of **1–3** in CD_2Cl_2 were studied by ^1H , $^{13}\text{C}\{^1\text{H}\}$, and $^{195}\text{Pt}\{^1\text{H}\}$ NMR spectroscopy. In the ^1H NMR spectra resonances for the $(\text{CH}_3)_2\text{N}$ and the ArCH_2N protons of the CH_2NMe_2 substituents were observed at $\delta = 3.06$ ppm and at $\delta = 4.06$ ppm, respectively, accompanied with characteristic satellites resulting from platinum coupling $^3J(\text{H}, \text{Pt})$. Only in **1** and **2** this coupling on the CH_2 protons could be resolved ($^3J(\text{H}, \text{Pt}) = 37\text{--}38$ Hz). The other platinum couplings with the protons of the CH_2 and CH_3 groups in these compounds appeared as a broad signal at the base of the singlet peaks. Furthermore the characteristic resonances of the olefinic protons were observed at $\delta = 6.3\text{--}7.5$ ppm with large coupling constants ($^3J(\text{H}, \text{H}) = 16$ Hz) indicative of a *trans* configuration. For **1**



Scheme 1. Synthetic route towards diethyl benzylphosphonate esters **9a–c**.

Reagents and conditions: i: (CHO)_n, 33% HBr/AcOH, 80 °C; ii: a) MeOH, H₂SO₄, reflux; b) LiAlH₄, THF, reflux; iii: 33% HBr/AcOH, rt; iv: Br₂, FeCl₃ (cat.), C₂H₄Cl₂, reflux; v: NBS, BPO, CCl₄, reflux; vi: P(OEt)₃, 110 °C.



Scheme 2. The air stable solids **1–3** were fully characterized by ¹H, ¹³C{¹H}, ¹⁹⁵Pt{¹H} NMR spectroscopy, elemental analysis, and high-resolution mass spectrometry.

(R = OMe) the resonances of these protons were found at much lower field (δ H_{trans} = 7.47/7.18 ppm), compared with the signals of **3** (R = Br), which were found at higher field (δ H_{trans} = 6.94/6.68 ppm), showing that these proton chemical shifts are affected by the nature of the substituent.

Also, in the ¹³C{¹H}, and the ¹⁹⁵Pt{¹H} NMR spectra of **1–3** the net electronic effect exerted by the substituents R on the conjugated system is directly reflected in the positions of the C_{ipso} (to platinum) carbon atom (δ ¹³C_{ipso} = 146–148 ppm), and the platinum NMR chemical shifts of the metal center (δ ¹⁹⁵Pt = –3149 to –3158 ppm) (Table 1). Going through from **1**, which contains three donating OMe groups, towards **3**, containing the, primarily, electron withdrawing Br groups, both resonances shift to lower field. This effect points to an electronic interaction between the central aromatic ring and the end bound organometallic fragment; i.e., electron density is shifted from the metal to the central core. For 4,4'-disubstituted stilbenoid Pt-pincers, ¹⁹⁵Pt chemical shifts of –3164 and –3158 ppm is found for the 4-MeO and H substituents, respectively [11]. The effect of the substituent on the ¹⁹⁵Pt chemical shift in the octupolar compounds is thus about equally large as in the stilbene-Pt pincers.

Table 1

Selected ¹³C{¹H} and ¹⁹⁵Pt{¹H} NMR data of 1,3,5-tri-R-2,4,6-tris[(4-(PtCl)(3,5-bis[(dimethylamino)methyl]styryl))benzene **1–3**.^a

Compound	1 (R = OMe)	2 (R = H)	3 (R = Br)
$\delta^{13}\text{C}_{\text{ipso}}\{^1\text{H}\}$	146.8	147.3	148.1
$\delta^{195}\text{Pt}\{^1\text{H}\}^b$	–3158	–3154	–3149

^a 0.024 M solutions in CD₂Cl₂; δ in ppm.

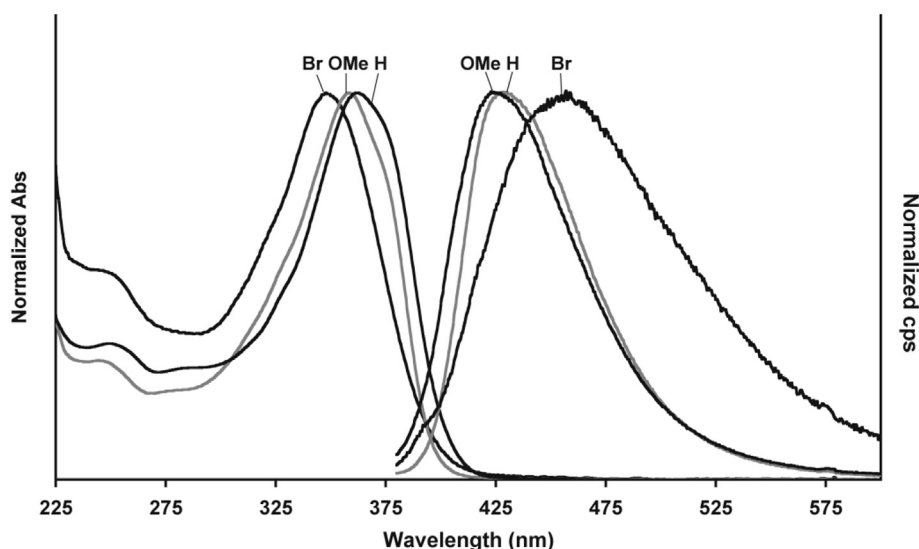
^b Na₂PtCl₆ as the external reference.

2.3. UV/Vis spectroscopy

The complexes **1–3** are freely soluble in dichloromethane, whereas they show a limited solubility in less polar solvents like diethyl ether (Table 2). As a result of the restricted solubility the absorption coefficient ϵ of the complexes was only determined in dichloromethane. The absorption spectra for **1–3** (Fig. 3, Table 2) show a weak band between 251 and 253 nm originating from the excitation of the singlet ground state (S₀) to a higher excited state (e.g. S₀ → S₂) [9,11,29]. A more intense lower energy band (S₀–S₁), is observed in the range of 343–364 nm. The position of the

Table 2
UV/Vis and fluorescence data of **1–3**.^a

Solvent	λ_{max} (nm)	λ_{fl} (nm) ^b	ϕ_{fl}	τ_{fl} (ns)	k_{r} ($\cdot 10^7 \text{ s}^{-1}$) ^c	k_{nr} ($\cdot 10^9 \text{ s}^{-1}$) ^d
1 (R = OMe)						
Acetonitrile	353	433	0.010	0.17	5.9	5.8
Dichloromethane	251 [22.7] 359 [90.2]	425	0.008	0.17	4.7	5.8
Tetrahydrofuran	361	422	0.006	0.14	4.3	7.1
Ethyl acetate	357	420	0.003	0.15	2.0	6.6
Diethyl ether ^e	358					
2 (R = H)						
Acetonitrile	356	444	0.020	0.19	10.5	5.2
Dichloromethane	253 [27.1] 362 [89.5]	428	0.015	0.16	9.4	6.2
Tetrahydrofuran	364	423	0.010	0.15	6.7	6.6
Ethyl acetate	346	420	0.006	0.15	4.0	6.6
Diethyl ether ^f						
3 (R = Br)						
Acetonitrile	343	467	0.0012	0.20	0.6	5.0
Dichloromethane	253 [29.1] 348 [65.3]	454	0.015	0.15	10.0	6.6
Tetrahydrofuran	354	465	0.0005	0.17	0.3	5.9
Ethyl acetate	348	467	0.0012	0.17	0.7	5.9
Diethyl ether ^f						

^a Lower energy absorption wavelength (nm) at room temperature in air-saturated solutions ($c \approx \cdot 10^{-5} \text{ M}$), absorption coefficient ϵ between brackets (ϵ in $\cdot 10^3 \text{ M}^{-1} \text{ cm}^{-1}$).^b Excitation wavelength 370 nm, argon flushed solutions at room temperature, $c \approx \cdot 10^{-6} \text{ M}$.^c $k_{\text{r}} = \phi_{\text{fl}}/\tau_{\text{fl}}$.^d $k_{\text{nr}} = (1 - \phi_{\text{fl}})/\tau_{\text{fl}}$.^e Restricted solubility.^f Insoluble.**Fig. 3.** Normalized UV/Vis (left) and emission spectra (right) of **1–3** in dichloromethane.

absorption band is found at the lowest wavelength for **3**, followed by **1** and **2**. Given that the Pt-Cl moiety behaves as an electron donor,[5] there is no clear relation with the donor-acceptor character of R. In that case the longest wavelength would be observed for the electron acceptor Br, followed by H and OMe. For **1** and **2** in all solvents, the absorption maxima are only slightly red-shifted (by 5–12 nm) in comparison to the transitions in stilbenoid Pt-Cl pincer compounds with the same R-group (i.e., the separate branches).[5] This suggests that there is only a limited electronic interaction between these branches. The absorption spectra of **1–3** show no distinct solvent polarity dependence (Table 2), indicating that the (vertical) electronic excitation is not accompanied by a substantial change in dipole moment. Similar behavior was observed for three-fold symmetric diphenylamino-substituted triphenylbenzene [30].

As reflected by their absorption coefficient of $\epsilon \approx 65\text{--}90 \cdot 10^3 \text{ M}^{-1} \text{ cm}^{-1}$ the absorption bands of **1–3** show intense absorption bands. These values are about two (for **3**) to three times (for **1** and **2**) larger than the value obtained for linear dipolar 4,4'-substituted stilbenoid pincer platinum complexes [11], which is in agreement with the factor found between the similar organic 4,4'-substituted stilbene and octupolar compounds (factor 2.7) [31].

2.4. Emission spectroscopy

The compounds are luminescent, and were therefore studied for their photophysical properties by determination of the fluorescence maxima (λ_{fl}), quantum yields (ϕ_{fl}) and excited state lifetimes (τ_{fl}). From these data the radiative (k_{r}) and non-radiative (k_{nr}) decay constants were calculated.

Emission spectra and excited state lifetimes were recorded in solvents of different polarity (Table 2). The emission spectra of **1–3** show a broad non-structured emission band in the range of $\lambda_{\text{fl}} = 420\text{--}467\text{ nm}$, and examples of the emission spectra in dichloromethane are depicted in Fig. 3. For compounds **1** and **2** a small bathochromic shift of the emission maximum with an increase in solvent polarity is observed. The occurrence of this positive solvatochromism reflects the formation of a polar or charge separated excited state. For **3** this behavior was not observed. The solvatochromism and Stokes' shifts are, however, not as large as observed for other threefold symmetric molecules like diphenylamino-substituted triphenylbenzene [30] and 1,3,5-methoxy-2,4,6-trisstyrylbenzene derivatives [13], confirming that only a limited extent of charge separation takes place. In view of the weaker donor and acceptor used in the present study this does not come as a surprise.

The complexes are only weakly luminescent, shown by the low quantum yields ($\Phi_{\text{fl}} = 0.0005\text{--}0.02$), with the lowest values found for **3**. Although one would expect that this may be caused by the heavy-atom effect (which favors intersystem crossing), the k_{r} and k_{nr} data indicate that it is rather the radiative part of the decay that is slower for **3** (with the exception of the data in dichloromethane). Alternatively, the very low Φ_{fl} for **3** may be caused by a fraction of non-emitting complexes that decay too fast to contribute to the measured τ_{fl} . The observation that radiative rate constants is of the order of 10^7 s^{-1} suggests that fluorescence is responsible for the radiative decay to the ground state (not phosphorescence). The relaxation process is, however, dominated by the non-radiative decay process which is two orders of magnitude larger than the radiative decay. Presumably the presence of the NCN-PtCl fragment favors non-radiative decay, which is likely to be caused by the heavy atom effect.

The fluorescence Stokes' shift, quantum yields and lifetimes of **1–3** are of the same order of magnitude as those of stilbenoid Pt pincer compounds [11], and hence their photophysics are roughly similar. In common with the amino substituted triphenylbenzenes, it is thus likely that a dipolar excited state is formed, which is localized on one of the three branches. In the excited state, energy transfer between the three branches may occur [32].

2.5. NLO-properties

A general drawback of the application of linear dipolar molecules in electro-optic devices is that they must be aligned parallel to the applied electric field to exhibit second-harmonic generation (SHG). Several techniques have been developed to align these molecules in a parallel fashion, opposing the tendency of dipoles to orient in an antiparallel pattern [33]. The problem can be overcome with the development of octupolar complexes, which have no net dipole moment. Therefore, octupolar materials containing NLO properties are very interesting for the application in electro-optic devices [31]. In this study the second-order hyperpolarizability β was determined for octupoles **1–3** using the hyper-Rayleigh scattering (HRS) technique [34,35], in dichloromethane solution. The obtained data are tabulated in Table 3. This table shows the measured values β_{HRS} , the only non-zero hyperpolarizability tensor

$\beta_{\text{xxx}} ((\beta_{\text{xxx}})^2 = \langle (21/8) \beta_{\text{HRS}} \rangle^2$, assuming D_{3h} symmetry) and the static (frequency independent) values $\beta_{\text{HRS}}(0)$. The latter ones were obtained by

$$\beta_{\text{HRS}}(0) = \beta_{\text{HRS}}(\omega) \frac{(\omega_{\text{max}}^2 - 4\omega^2)(\omega_{\text{max}}^2 - \omega^2)}{\omega_{\text{max}}^4}$$

where $\beta_{\text{HRS}}(0)$ is the hyperpolarizability at the used laser frequency ω , and ω_{max} is the frequency at the absorption maximum of the NLO-active compound [36].

The largest β values are found for **2** ($R = \text{H}$). The β_{HRS} and β_{xxx} values are as high as 870 and $1410 \times 10^{-30}\text{ esu}$, respectively. However, one should not forget that resonance enhancement occurs for **1–3**, as their optical transitions are relatively close to the used laser wavelength of 800 nm. Correction with the oversimplified two-level model [36] yields the numbers $36\text{--}125 \times 10^{-30}\text{ esu}$. Because of the closeness of the second-harmonic wavelength (400 nm) to the resonance wavelength of the lowest-energy absorption (approximately 360 nm in CH_2Cl_2), the resulting static $\beta(0)$ values are underestimated. Nevertheless, the resulting values still are of the same order of magnitude as the highest β 's of other transition metal containing NLO-complexes, viz. metal acetylide and vinylidene complexes ($\beta(0)$ values up to $406 \times 10^{-30}\text{ esu}$ [18], and alkynyl ruthenium dendrimers ($\beta(0)$ values up to $220 \times 10^{-30}\text{ esu}$) [20]. They compare favourably to subphthalocyanines, for which $\beta_{\text{HRS}}(0)$ values of $10\text{--}86 \times 10^{-30}\text{ esu}$ were reported [37]. Recently, a very large value of $1700 \times 10^{-30}\text{ esu}$ (static value $1300 \times 10^{-30}\text{ esu}$ was reported for an octupolar bis(porphyrinato)terbium(III) complex [21].

It is of interest to also compare the data for **1–3** with those of the stilbenoid pincer platinum complexes [6]. For these compounds $\beta(0)$ values were found to range from 46 ($R = \text{SiMe}_3$) to $216 \times 10^{-30}\text{ esu}$ ($R = \text{I}$; this value was much larger than for the other substituents, which might be related to the large polarizability of the iodine substituent). The optical nonlinearities for the tris-stilbene analogues are thus of comparable magnitude, the latter compounds having the advantage of a vanishing static dipole moment.

In comparison to **1** and **3**, the β values for compound **2** are noticeably high. Thus, the highest value is found for the compound lacking a donor or acceptor group at the central core, which supports the idea that the charge transfer characteristics are not decisive in the behavior of C_3 symmetric compounds [17]. The subtle difference in the absorption characteristics is responsible (Table 2 and Fig. 1, notice the strong red-shifted shoulder for **2**), as it has been noticed that “dispersion overwhelms charge transfer in determining the magnitude of the first hyperpolarizability” in octupoles [17]. A more quantitative analysis of this effect would require the detailed description of the absorption bands based on band fitting and the application of the Thomas-Kuhn Sum rules, together with more experimental data of the strong dispersion of the first hyperpolarizability close to the resonance wavelength [17]. This would allow a much finer dispersion analysis than the crude two level model.

3. Conclusions

The electronic properties of the octupolar platinum complexes do not differ very much from those of the separate branches bearing the same substituents (i.e., the corresponding stilbenoid Pt-Cl pincer compounds). The effect of the substituent on the ^{195}Pt NMR chemical shift in the octupolar compounds is about as large as in the stilbene-Pt pincers, while UV/Vis bands of the octupolar compounds are only slightly red-shifted. This indicates that there is only a limited electronic interaction between the individual

Table 3
HRS results of R-trisstilbene pincers. Values in 10^{-30} esu .^a

Complex	β_{HRS}	β_{xxx}	$\beta_{\text{HRS}}(0)$
1 ($R = \text{OMe}$)	430(± 45)	700(± 70)	66(± 7)
2 ($R = \text{H}$)	870(± 105)	1410(± 170)	125(± 15)
3 ($R = \text{Br}$)	183(± 19)	300(± 30)	36(± 4)

^a Solution in CH_2Cl_2 , laser 800 nm.

branches of **1–3**. Furthermore, the fluorescence properties (Stokes shift, quantum yields and lifetimes) of **1–3** also are similar to those of the stilbenoid Pt pincer compounds. This can be explained by formation of a dipolar excited state, which is localized on one of the three branches. However, energy transfer between the three branches may occur.

Hyperpolarizabilities β of the octupolar compounds are however higher than those of Pt-stilbene compounds. In this respect, the octupolar nature of the electronic system really makes a difference; the reported values are among the highest for organometallic compounds. It is furthermore of interest that the highest hyperpolarizability was found for the compound lacking a donor or acceptor group at the central core, which supports the idea that dispersion rather than charge transfer is important in the NLO-behavior of C_3 symmetric compounds.

All in all, it can be concluded that the introduction of the NCN-pincer platinum fragment as a substituent led to the development of new organometallic octupolar systems with attractive NLO properties.

4. Experimental

General: All reactions involving air- or moisture-sensitive reagents were performed by standard Schlenk techniques unless stated otherwise. Toluene, pentane, THF and Et₂O were distilled from Na/benzophenone, CH₂Cl₂ was distilled from CaH₂ and triethylamine was distilled from KOH prior to use. The platinum precursor [PtCl(NCN-CHO-4)], and the *para*-substituted diethyl benzylphosphonates **8** were prepared according to published procedures (see text) [11,38]. All other reagents were obtained commercially and used without further purification. ¹H and ¹³C{¹H} NMR spectra were recorded at 25 °C on Bruker AC 300 NMR or Varian Inova 300 spectrometers (operating at 300 and 75 MHz, respectively), chemical shifts are depicted in ppm and referenced to residual solvents resonances. ¹⁹⁵Pt{¹H} NMR spectra were recorded on a Varian Inova 300 MHz NMR spectrometer (operating at 64.4 MHz) and referenced to external Na₂PtCl₆ (1 M in D₂O, δ = 0 ppm) [39].

Elemental analyses were performed by Kolbe, Mikroanalytisches Laboratorium (Mülheim, Germany). ES-MS spectra were obtained from the Biomolecular Mass Spectrometry Department of the Utrecht University. Infra-red spectra were recorded with a Perkin Elmer Spectrum one FT-IR spectrometer. UV spectra were collected on Cary 1 or Cary 5 spectrophotometers in spectrophotometric grade solvents. Fluorescence emission spectra were obtained on a Spex Fluorolog spectrofluorimeter, equipped with a Spex 1680 double excitation monochromator, a Spex 1681 emission monochromator and a Spex 1911F detector. Fluorescence spectra were corrected for the detector spectral response with the aid of a correction file provided by the manufacturer. Fluorescence quantum yields were determined relative to 9,10-diphenylanthracene (Φ_F = 0.90, excitation wavelength 370 nm) [40]. Solvents used for fluorescence measurements were of spectrophotometric grade (Acros).

Lifetime measurements were performed by using a Pico Quant PDL 800-B laser as the excitation source (λ_{exc} = 406 nm, 55 ps pulse width, 2.5–40 MHz repetition rate). The luminescence was collected through a focusing lens, filtered through a crossed polarizer and a combination of suitable optical cut-off filters, dispersed by a 0.1 m monochromator (1350 lines/mm grating, blazed at 500 nm) and detected by a fast Hamamatsu photomultiplier tube (PMT) (H5738P-01). The PMT signal was amplified by an inverting preamplifier (PAM-102-T – PicoQuant) and used as the start input for a Time Harp 200 multi-channel computer card, which was synchronized with the laser pulse *via* the stop input. The

decay curves were obtained by time correlated single photon counting (TCSPC) *via* time-to-amplitude conversion (TAC). The ratio of stop to start pulses was kept low (below 0.04) to assure good statistics. The instrument response function (IRF) was measured by using a diluted suspension of silica particles (LUDOX) as the scattering medium and the same experimental conditions used for the fluorescence decay measurements. The raw data was deconvoluted from the IRF and analyzed by a fluorescence decay analysis software (Fluofit 3.3). The instrumental resolution was 30 ps (10% of the IRF FWHM).

Accurate hyperpolarizabilities β were determined by hyper-Rayleigh scattering at 800 nm as described elsewhere [41]. Individual samples in dichloromethane were measured at five different concentrations and different modulation frequencies, in order to exclude contributions of multiphoton fluorescence from the nonlinear scattering signal.

4.1. General procedure octupolar pincer compounds **1–3**

In a dry Schlenk tube, [PtCl(NCN-CHO-4)] (**10**) (3 equiv.) and the appropriate benzylphosphonate ester **9a–c** (1 equiv.) were dissolved in dry degassed THF (10–15 mL). While stirring, *t*-BuOK (6 equiv.) was added to the reaction mixture, under a nitrogen outflow, which directly caused a strong color change from light yellow to orange of the reaction mixture. After stirring at RT (3 h), the mixture was quenched at 0 °C by the subsequent addition of ice and an aqueous NaCl solution (to prevent halogen abstraction on the Pt center). The formed precipitate was isolated by filtration through a glass filter. The residue was dissolved in dichloromethane and dried using MgSO₄, filtered, and evaporated to leave the crude product. The crude product was purified by precipitation out of a small amount of dichloromethane by the addition of pentane, and isolated after centrifugation.

4.1.1. 1,3,5-Tri-OMe-2,4,6-tris[(4-(PtCl)(3,5-bis[(dimethylamino)methyl]styryl))-benzene (**1**)

1,3,5-Trimethoxy-2,4,6-tris[(diethoxyphosphoryl)methyl]benzene **9a** (92 mg, 0.15 mmol), **10** (200 mg, 0.44 mmol). Product **1** was isolated as a light-yellow powder (196 mg, 0.13 mmol, 87%). ¹H NMR (300 MHz, CD₂Cl₂): δ = 7.47 (d, ³J(H,H) = 16.7 Hz, 3H; *trans* CH=CH), 7.18 (d, ³J(H,H) = 16.5 Hz, 3H; *trans* CH=CH), 7.05 (s, 6H; ArH), 4.06 (s, ³J(H,Pt) = 38.2 Hz, 12H; NCH₂), 3.70 (s, 9H, OCH₃), 3.06 (s, ³J(H,Pt) = broad, 36H; NCH₃); ¹³C{¹H} NMR (75 MHz, CD₂Cl₂): δ = 156.6, 146.8 (*Cipso*), 144.4, 134.7, 134.5, 122.4, 117.8, 117.0, 78.0 (NCH₂), 60.3 (OMe), 54.6 (NCH₃); ¹⁹⁵Pt{¹H} NMR (64 MHz, CD₂Cl₂): δ = –3158; IR (ATR): $\tilde{\nu}$ = 3464, 2981, 2918, 1622, 1585, 1450, 1398, 1334, 1300, 1270, 1235, 1189, 1141, 1098, 1004, 970, 945, 879, 835, 706, 668 cm^{–1}; MS (ES+; CH₂Cl₂) *m/z*: 1504.40 [M+H]⁺; elemental analysis calcd (%) for C₅₁H₆₉Cl₃N₆O₃Pt₃ (1505.72): C 40.68, H 4.62, N 5.58; found: C 40.76, H 4.65, N 5.43.

4.1.2. 1,3,5-tris[(4-(PtCl)(3,5-bis[(dimethylamino)methyl]styryl))benzene (**2**)

1,3,5-Tris[(diethoxyphosphoryl)methyl]benzene **9b** (66 mg, 0.12 mmol), **10** (200 mg, 0.44 mmol). Product **2** was isolated as an off-white powder (162 mg, 0.11 mmol, 92%). ¹H NMR (300 MHz, CD₂Cl₂): δ = 7.51 (s, 3H; ArH), 7.13 (d, ³J(H,H) = 16.7 Hz, 3H; *trans* CH=CH), 7.07 (d, ³J(H,H) = 16.7 Hz, 3H; *trans* CH=CH), 7.04 (s, 6H; ArH), 4.06 (s, ³J(H,Pt) = 37.3 Hz, 12H; NCH₂), 3.06 (s, ³J(H,Pt) = broad, 36H; NCH₃); ¹³C{¹H} NMR (75 MHz, CD₂Cl₂): δ = 147.3 (*Cipso*), 144.4, 139.1, 133.0, 130.8, 125.6, 123.0, 118.0, 77.9 (NCH₂), 54.6 (NCH₃); ¹⁹⁵Pt{¹H} NMR (64 MHz, CD₂Cl₂): δ = –3154; IR (ATR): $\tilde{\nu}$ = 3456, 3012, 2916, 1625, 1579, 1450, 1399, 1337, 1270, 1230, 1179, 1140, 1085, 1014, 958, 870, 839, 708, 689 cm^{–1}; MS (ES+; CH₂Cl₂) *m/z*: 1415.37 [M+H]⁺; elemental analysis calcd (%)

for $C_{48}H_{63}Cl_3N_6Pt_3$ (1415.65): C 40.72, H 4.49, N 5.94; found: C 40.88, H 4.43, N 5.79.

4.1.3. 1,3,5-Tri-Br-2,4,6-tris[(4-(PtCl)(3,5-bis[(dimethylamino)methyl]styryl)]benzene (**3**)

1,3,5-Tribromo-2,4,6-tris[(diethoxyphosphoryl)methyl]benzene **9c** (90 mg, 0.12 mmol), **10** (166 mg, 0.37 mmol). Product **3** was isolated as a light-yellow powder 145 mg (0.09 mmol, 75%). 1H NMR (300 MHz, CD_2Cl_2): δ = 7.04 (s, 6H; ArH), 6.94 (d, $^3J(H,H)$ = 16.5 Hz, 3H; *trans* CH=CH), 6.68 (d, $^3J(H,H)$ = 16.5 Hz, 3H; *trans* CH=CH), 4.06 (s, $^3J(H,Pt)$ = broad, 12H; NCH_2), 3.06 (s, $^3J(H,Pt)$ = broad, 36H; NCH_3); $^{13}C\{^1H\}$ NMR (75 MHz, CD_2Cl_2): δ = 148.1 (Cipso), 144.5, 140.3, 138.2, 131.9, 125.9, 123.6, 118.1, 77.9 (CH_2N), 54.6 (NCH_3); $^{195}Pt\{^1H\}$ NMR (64 MHz, CD_2Cl_2): δ = -3149; IR (ATR): $\tilde{\nu}$ = 3463, 2980, 2914, 1626, 1585, 1449, 1399, 1339, 1295, 1270, 1230, 1086, 1014, 959, 875, 838, 668 cm^{-1} ; MS (ES⁺; CH_2Cl_2) m/z : 1653.08 $[M+H]^+$; elemental analysis calcd (%) for $C_{48}H_{60}Br_3Cl_3N_6Pt_3$ (1652.34): C 34.89, H 3.66, N 5.09; found: C 34.75, H 3.76, N 4.96.

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Appendix A. Supplementary data

NMR data of compounds **1–3**.

Supplementary data related to this article can be found at <https://doi.org/10.1016/j.jorganchem.2017.12.028>.

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