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Second-Order Nonlinear Optical Properties of Push−Pull Bis(phenylethynyl)benzenes and Unsymmetric Platinum Bis(phenylacetylide) Complexes

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Donor−acceptor substituted π-conjugated organics possessing low-lying charge-transfer excited states are known to exhibit large second-order optical nonlinearities.[1] Consequently, these materials have received considerable attention due to their potential applications in optoelectronics, telecommunications, and optical storage devices.[1,2] The vast majority of known nonlinear optical (NLO) chromophores are based on substituted benzene, stilbene, Schiff base, and azobenzene derivatives. Among these, push−pull stilbene compounds have been shown to exhibit large first molecular hyperpolarizabilities (β).[3] Several thiophene-based stilbene analogues have also been exploited as a means to overcome the unfavorable loss of aromaticity in the charge-separated excited state which is inherent in the benzene derivatives. These compounds have been reported to possess significantly enhanced nonlinearities.[4,5] Further work on the extension of the π-conjugation connecting the donor and acceptor moieties, as exemplified by the polyene system, have resulted in exceptionally large β values.[6,7] However, an unavoidable consequence for β enhancement in these compounds is the red-shift in their optical absorption into the visible part of the spectrum, thus limiting their practical application in this frequency range. Recent studies on some unsymmetric tolans[8−10] have indicated that the presence of the $C{\equiv}C$ bridging unit reduces significantly the molecular charge-transfer character and thus gives rise to materials with improved optical transparency.[9,10] However, the penalty for this transparency is a decrease in β for the tolan systems. Improvement in the second-order nonlinearity while maintaining good optical transparency can be envisaged for the tolan molecule core via lengthening of the π-conjugated network. We have undertaken two different approaches to extending the π-electron delocalization in this system: (1) via $d\pi{-}p\pi$ interaction utilizing a bis(phosphine) platinum moiety as the central element bridging the donor, phenylethynyl, and the acceptor, phenylethynyl, fragments in a trans-disposed linear arrangement; (2) incorporation of an additional phenylethynyl unit into the $p\pi$ backbone. We have reported recently the synthesis and characterization of three unsymmetric 1,4-(*p*-R-phenylethynyl)(*p*-nitrophenylethynyl)benzenes (R = MeO (**6a**), MeS (**6b**), NMe_2 (**6d**)).[11] In the present work, the same synthetic methodology was used to prepare the NH_2 derivative and the four cyano acceptor analogues.[12] The *trans*-bis(dimethylphenylphosphine)platinum complexes (**8a**, **8b**) were prepared as described previously.[13] The linear and nonlinear optical properties of these chromophores have also been investigated and are reported herein, allowing a comparison between all-organic and metal-containing systems to be made.

Compounds **5a−d** and **6a−d** were prepared in a controlled stepwise manner via the iodo intermediates **3** and **4**, respectively. Scheme 1 illustrates the reaction sequence involving the coupling reaction of 4-cyanophenylethyne (**2a**) with 1,4-diiodobenzene (**1**) in the presence of catalytic amounts of $PdCl_2(PPh_3)_2$ and CuI to afford the monocoupled product 1-iodo-4-(*p*-cyanophenylethynyl)benzene (**3**). The reaction was carried out by dropwise addition of an amine solution of **2a** to a reaction mixture containing the Pd and Cu catalysts

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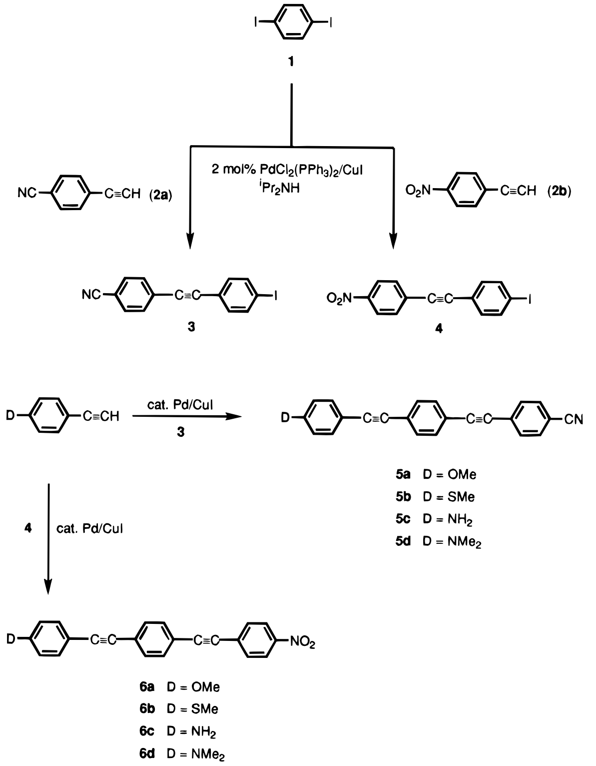
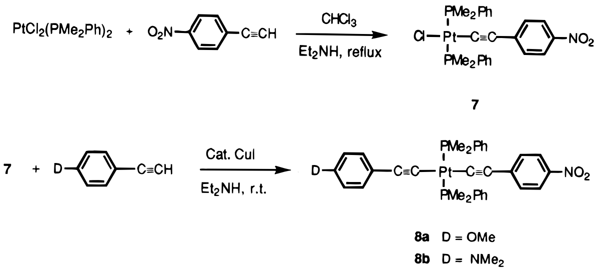
Scheme 1. General Synthetic Route to Unsymmetric D/A Bis(phenylethynyl)benzenes 5a−d and 6a−d



Scheme 2. Synthesis of Unsymmetric D/A Platinum Bis(acetylide) Complexes 8a,b



and an excess of **1** (**1**:**2a** = 3/1) to suppress the formation of the symmetric bis-coupled product. In subsequent reactions, **3** was allowed to react with various π-donor para-D-substituted phenylethynes (D = MeO (**2c**), MeS (**2d**), NH_2 (**2e**), NMe_2 (**2f**)) to give the unsymmetric D/CN bis(phenylethynyl)benzenes (BPEBs, **5a**−**d**). Similarly (Scheme 1), the nitro intermediate **4**, and the D/NO_2 BPEBs (**6a**−**d**) were obtained from the coupling of **1** with the corresponding 4-nitrophenylethyne (**2b**), followed by coupling with *p*-D-substituted phenylethynes (**2c**−**f**).

The unsymmetric Pt complexes[13] were prepared (Scheme 2) via attachment of the two acetylides sequentially. The monoacetylide species *trans*-[Pt(PMe_2Ph)$_2$-(Cl)($C{\equiv}CC_6H_4$-4-NO_2)] (**7**) was obtained by refluxing a solution of [Pt(PMe_2Ph)$_2Cl_2$] and *p*-nitrophenylethyne in $CHCl_3$ in the presence of Et_2NH. Compound **7** then reacts further with donor alkynes such as *p*-methoxyphenylethyne and *p*-(dimethylamino)phenylethyne in the presence of Et_2NH and CuI to give **8a** and **8b**, respectively.

Physical data for compounds **5a**−**d**, **6a**−**d**, and **8a**,**b** are summarized in Table 1. Compounds **5a**−**d** and **6a**−**d** have strong absorptions in the near-UV and emission in the visible regions. The solution UV−vis absorption spectra for these compounds are very similar and are characterized by two intense broad bands in the region 316−384 nm with large extinction coefficients. The broad band at the longer wavelength, which vanishes upon protonation with HCl, is assigned as the intramolecular charge-transfer (ICT) transition. The high-energy band is only slightly affected by HCl and thus is assigned as a $\pi-\pi^*$ transition. Similar observations were reported by Stiegman et al. for the tolan derivatives.[9a] For the all-organic series, the ICT absorption and emission bands are red-shifted with increasing donor strength in the order of MeO < MeS < NH_2 < NMe_2 for a fixed acceptor. Likewise, the absorption and emission maxima for the compounds bearing the stronger accepting group, NO_2, are shifted bathochromically relative to the CN analogues. Surpringly, absorption for the MeO/NO_2 complex (**8a**) is much more intense and occurs at a slightly longer wavelength than the NMe_2/NO_2 derivative (**8b**).

The first hyperpolarizabilities of these compounds (Table 1) were determined by the electric field induced second harmonic generation (EFISH) method. All measurements were performed in $CHCl_3$ solutions at a fundamental wavelength of 1.064 μm. It is apparent from Table 1 that the magnitude of $\mu\beta$ increases according to the donor strength in the order MeO < MeS < NH_2 < NMe_2 for the CN/D BPEBs (**5a**−**d**), and for the platinum complexes, $\mu\beta$ value for the NMe_2/NO_2 derivative (**8b**) is greater than twice that of the MeO/NO_2 (**8a**) analogue. Similarly, the $\mu\beta$ values observed for the NO_2 analogues (**6a**−**d**) follow the same basic trend in which $\mu\beta$ increases with the strength of the donor group. Accounting for dispersive enhancement according to the two-state approximation,[14] $\mu\beta(0)$ values are 120×10^{-48} (**5a**), 130×10^{-48} (**5b**), 180×10^{-48} (**5c**), and 370×10^{-48} esu (**5d**) for the CN series and 200×10^{-48} (**6a**), 180×10^{-48} (**6b**), 310×10^{-48} (**6c**), and 510×10^{-48} esu (**6d**) for the NO_2 series. As expected, $\mu\beta(0)$ values are larger for the latter series due to the greater acceptor strength of NO_2 relative to CN. Moderate $\mu\beta(0)$ values of 130×10^{-48} (**8a**) and 290×10^{-48} esu (**8b**) were obtained for the Pt bis(acetylide) complexes. For comparison, $\mu\beta(0)$ values (calculated from data measured at 1.907 μm)[9b] for the shorter MeS, H_2N, and Me_2N tolan analogues are 51, 87, and 144×10^{-48} esu for the CN series and 52, 66, 107, and 217×10^{-48} esu for the MeO, MeS, H_2N, and Me_2N of the NO_2 series. Thus, it is clear that extension of the π-conjugation in the tolan chromophores by one phenylethynyl unit resulted in a significant enhancement of $\mu\beta$.[15] In contrast, only moderate improvement in $\mu\beta$ was observed for the Pt bis(acetylide) complexes versus the tolan compounds. It is also worth noting that even though the Pt bis(acetylide) complex (**8b**) has the largest $\beta(0)$ value, its $\mu\beta(0)$ is, in fact, smaller in comparison to the bis(phenylethynyl)benzene (**6d**) due to the inherent larger dipole moment exhibited by the latter. However, the Pt center is a reasonably efficient component from

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Table 1. Melting Points, Absorption, and Nonlinear Optical Data for 5a–d, 6a–d, and 8a,b

molecule	mp (°C)	λ_{max} (nm) (log ϵ)[a]	μ_{calc} (D)[c]	μ_{exp} (D)[c]	$\mu\beta^{a,b}$ (10^{-48} esu)	β (10^{-30} esu)	$\mu\beta(0)^{a}$ (10^{-48} esu)	$\beta(0)$ (10^{-30} esu)
MeO/CN (**5a**)	226–228	340(4.75)	7.4	6.3	240	38	120	19
MeS/CN (**5b**)	238–240	344(4.77)	9.0	8.6	250	29	130	15
NH_2/CN (**5c**)	284–286	350(4.66)	9.4	9.0	420	47	180	20
NMe_2/CN (**5d**)	283–285	376(4.60)	8.2	11	840	76	370	34
MeO/NO_2 (**6a**)	210–213	358(4.56)	7.4		400	54[d]	200	27[d]
MeS/NO_2 (**6b**)	224–226	362(4.50)	9.0	7.5	380	51	180	24
NH_2/NO_2 (**6c**)	285–287	370(4.55)	10.3	12	680	57	310	26
NMe_2/NO_2 (**6d**)	286–288	384(4.40)	9.0	10	1200	120	510	51
MeO–Pt–NO_2 (**8a**)	165–167(dec)	386(3.88)		5.0	310	62	130	26
NMe_2–Pt–NO_2 (**8b**)	196–197(dec)	378(1.92)		5.3	670	126	290	55

[a] All measurements were carried out in $CHCl_3$ except for **8a**,**b**, which were done in CH_3CN. [b] EFISH measurements were done at 1.064 μm. [c] Reference 17. [d] Results based on calculated μ.

which to prepare conjugated chains for nonlinear optical materials.

More importantly, compounds **5a–d** and **6a–d** have optical absorption maxima below 400 nm. For the MeO/NO_2 (**6a**) and MeS/NO_2 (**6b**) compounds, λ_{max} is almost identical with that of the corresponding tolan derivatives,[10] whereas in the case of the NH_2/NO_2 (**6c**) and NMe_2/NO_2 (**6d**), λ_{max} actually undergoes a blue-shift of ca. 10 and 30 nm, respectively.[9b] In contrast, the CN series (**5a–d**) display slight bathochromic shifts of 3–12 nm in comparison to the tolan derivatives.[9b] The nonlinearity/transparency tradeoff for this class of compounds can be further appreciated by comparison to the well-known dyes such as (dimethylamino)nitrostilbene (DANS) ($\beta(0) = 55 \times 10^{-30}$ esu, $\lambda_{max} = 427$ nm in $CHCl_3$) and disperse red 1 (DR1) ($\mu\beta(0) = 500 \times 10^{-48}$ esu, $\lambda_{max} = 455$ nm). In addition, the BPEB compounds are quite thermally stable. For example, thermal analysis (TGA) of the NMe_2/NO_2 (**6d**) compound showed a mere 8% weight loss up to 290 °C. Thus, taken as a whole, the bis(phenylethynyl)benzene structure represents an excellent molecular π-framework for efficient second-order nonlinearity with good optical transparency in the visible region and good thermal stability.

In conclusion, we have demonstrated a general route to two series of donor–acceptor bis(phenylethynyl)benzenes and the unymmetric Pt bis(acetylide) complexes. Preliminary NLO studies indicate that these extended system are efficient chromophores with sizeable $\mu\beta$ values. Their thermal stability and transparency combine to make the BPEBs attractive for future development. The photophysics of these compounds is currently under investigation to probe the efficiency of the intramolecular electron-transfer processes and to gain further insight into the nature of their excited states.[16]

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