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A Triazine-Based Multi-Branched Platinum Acetylide Complex: Synthesis and Photophysical Properties

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Abstract: A triazine-based multi-branched platinum(II) acetylide complex was synthesized and fully characterized. The photophysical properties, electrochemical properties and first order hyperpolarizability were studied.

Keywords: Donor-acceptor structure, first order hyperpolarizability, multi-branched platinum (II) acetylide, photophysical properties.

INTRODUCTION

Organic molecules containing donor-acceptor structures always show high second-order nonlinear optical effect [1], and several groups also reported the two-photon absorption effect of these kind of molecules as optical limiting materials and up-conversion materials [2-3]. A significant conclusion from the previous work could be made that chemicals with donor-acceptor structures such as D-A, D-A-D, D-π-A, D-π-D, and multi-branched structures generally exhibit excellent two-photon absorption properties, and the two-photon absorption cross sections can be increased by extending the molecular conjugated system or incorporating multi-dipole structures into the molecules [4-7]. In addition, molecules containing heavy metal ions and rigid structure always exhibit large reverse saturable absorption due to the enhancement of the intersystem crossing from the first singlet excited state to the first triplet excited state [8, 9]. These conclusions can provide helpful guidelines for designing materials with large overall nonlinear optical properties.

Platinum acetylides exhibit high linear transmission and high nonlinear absorption over the visible to near infrared spectral region [10-11]. Could molecules exhibit high second-order nonlinear optical effect and the third-order nonlinear optical properties (including two-photon absorption and reverse saturable absorption) at the same time when the donor-acceptor structure and the multi-branched structure are introduced into a platinum acetylide complex? And how the second-order nonlinear optical effect and the third-order nonlinear optical property affect each other corresponding to the structure of the organic molecules? There are few papers discussed the questions clearly according to our learning.

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In order to address these questions, a triazine-based multi-branched platinum(II) acetylide complex containing donor-acceptor structures (compound **1**) was synthesized and characterized by ^{1}HNMR, MS and elemental analysis in this paper. The photophysical properties, electrochemical properties and the first order hyperpolarizability were preliminary studied, and the detailed studies of the other properties, such as time-resolved luminescence and nonlinear optical properties, will be done in the near future.

RESULTS AND DISCUSSION

The synthetic route to compound **1** was shown in Scheme **1**. Compounds **2** to **5** were synthesized according to the literatures [12-15]. **3** was prepared using **2** and 4-propylphenylacetylene, which was synthesized via Sonogashira reaction from 1-iodo-4-propylbenzene, as starting materials. **6** was prepared by the condensation reaction of **4** and **5** under basic conditions in methanol. **1** was synthesized by treating **3** with **6**.

The strong absorption band of **1** at 420 nm (Fig. **1** up) can be assigned to the interligand π-π* transition. The weak absorption band at 362 nm can be assigned to π-π* transition of the aryl rings. The weak absorption of **1** above 450 nm provides a wide observation window for the application in optical limiter. The maximum excited emission at 420 nm of **1** appears at 513 nm with a fluorescence quantum yield (ϕ) of 0.063 relative to quinine sulfate (in 0.5M H_2SO_4 solution) [16]. The low fluorescence quantum yield indicated the possibility of the high quantum yield from S_1 to T_1. However, the phosphorescence of **1** at room temperature was not observed. Detailed research will be done soon. The excitation spectrum of **1** reflects that the fluorescence band at 513 nm is ascribed to the intraligand π*-π transition.

1 exhibited an oxidation potential at 1.05 V vs Ag/AgCl attributed to a metal-centered Pt (IV/II) oxidation process

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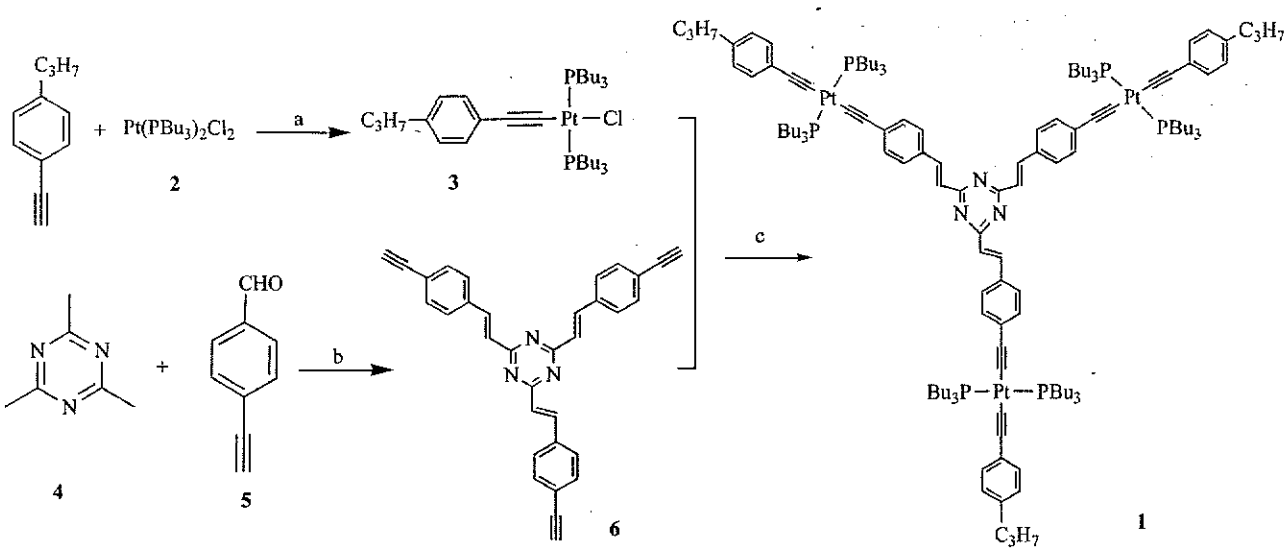

Scheme 1. Condition and reagent. (a)CuI, TEA, rt; (b)KOH, CH_3OH; (c) CuI, THF, rt.

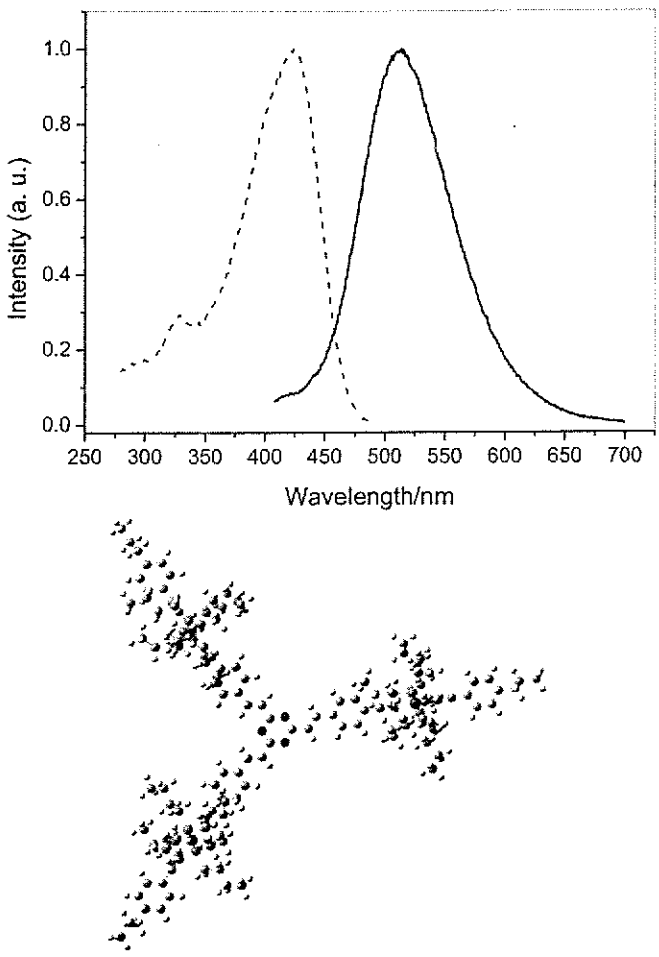

Fig. (1). Normalized emission spectrum (solid line) and absorption spectrum of **1** (dash line) in chloroform at room temperature and the optimized molecular structure of **1** by Gaussian 03.

and an irreversible reduction potential at -1.20 V vs Ag/AgCl assigned to the reduction of the coordinated ligand [17]. The electrochemical energy gap ($E_{g,ec}$ = 2.25 eV) is much similar to the value of $E_{g,opt}$ (2.45 eV), which is calculated from the absorption onset of **1** in chloroform [18].

The stereo structure of **1** was optimized using the density functional theory (DFT) at 6-31g level for C, H, N, P atoms and lans2dz level for Pt atom level, all the calculations were performed with the Gaussian 03 software [19]. As shown in (Fig. **1**) (down), the six benzene rings and the triazine ring in **1** are co-planar along each long-axis of vinyl, benzyl, acetylenyl, Pt, acetylenyl, and benzyl groups. Each Pt (II) center is square planar with the two phosphorus atoms *trans-* to each other. These results show that **1** has great structural rigidity and coplanarity, which are benefit for the transition from S_1 to T_1.

The first-order polarizability can be determined by the solvatochromism method [20]. The simple expression of the first-order polarizability is shown in Eq. 1: [21]

$$\beta_{xxx}(2\omega)=3/2\ \hbar^2\mu_{eg}^2\ (\mu_e - \mu_g)\ \omega_{eg}^2 / (\omega_{eg}^2-\omega^2)(\omega_{eg}^2 - 4\omega^2) \quad (1)$$

Where ω_{eg} is the frequency of the transition from the ground state to the first excited state, μ_{eg} is the transition dipole moment between the ground state and the excited state, μ_g is the permanent dipole moment of the ground state, μ_e is the permanent dipole moment of the excited state, and ω is the laser frequency. ω_{eg}, found from the absorption band maximum of **1**, is 4.50×10^{15} s^{-1}. μ_{eg}, gotten from the area under the absorption band, [22] is calculated to be 7.18×10^{-17} esu·cm. The value of μ_e - μ_g could be derived from Eq. (2) to (4).

$$\zeta_a - \zeta_f = A + B\ (BK) \quad (2)$$

$$B=2\ (\mu_e - \mu_g)^2/hca^3 \quad (3)$$

$$(BK)=[(\varepsilon-1)/(2\varepsilon+1)-(n^2-1)/(2\ n^2+1)]/[1-(n^2-1)\ /(2\ n^2+1)]^2\ [1-(\varepsilon-1)/(2\varepsilon+1)] \quad (4)$$

Where ζ_a -ζ_f is the Stokes shift in wave number [23]. A is the radius of a spherical cavity in the solvent occupied by the molecule and 10.02 Å was used in the calculation [24]. $\varepsilon$is the dielectric constant of solvent, n is the refractive index of solvent. BK is the Bilot-Kawski value of the solvent. The parameters of **1** in five selected solvents are listed in Table **1**. The relationship between BK values and stoke shifts (Fig. **2**) is linear with a slope (B) of 2548.67 cm^{-1}. μ_e - μ_g, derived from Eq.3, is 5.06×10^{-18} esu·cm. The first-order polarizabil-

Table 1. The Parameters of 1 Determined in Five Selected Solvents

Solvents	Benzene	Chloroform	THF	Methanol	Acetonitrile
$\nu_{OD}(cm^{-1})$	24272	23641	24331	24390	24272
$\nu_{ex}(cm^{-1})$	21786	19646	20408	19646	19417
$\triangle\zeta(cm^{-1})$	2486	3995	3923	4744	4855
BK	0.0036	0.3710	0.5491	0.8547	0.8631

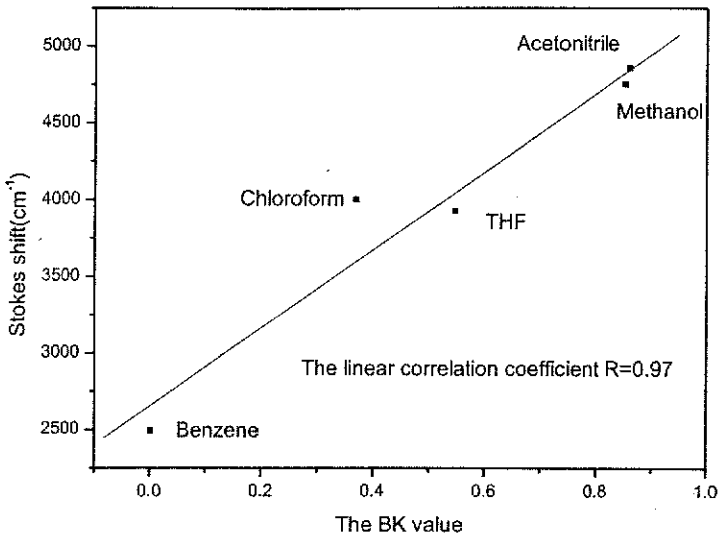

Fig. (2). The relationship between BK and ζ of **1** in different solvents.

ity $|\beta_{xxx}|$ of **1** is calculated to be 7.81×10^{-29} cm^5/esu by substituting the values of ω_{eg}, μ_{eg}, and μ_e - μ_g into Eq. 1.

Such a compound may be a promising nonlinear material. The syntheses and properties of more compounds are under investigation.

EXPERIMENTS

Materials and Methods

Silica Gel (GF254), 2-methylbut-3-yn-2-ol, K_2PtCl_4, $Pd(PPh_3)_2Cl_2$, PPh_3, CuI, $P(nBu)_3$, 4-propyl-phenylacetylene and 4-bromobenzaldehyde are all commercial available products and be used without more purification. $Pt(PBu_3)_2Cl_2$ (**2**) and 2,4,6-trimethyl-1,3,5-triazine (**4**) were prepared according to literature methods [14, 24]. ^{1}HNMR spectra were recorded with a 400 MHz Varian spectrometer. MALDI-TOF mass spectra were measured on AXIMA-CRF system. Elemental analyses were carried on a Flash EA 1112 elemental analyzer (Thermo Electron SPA, Italy).

$(Bu_3P)_2PtCl_2$ (2) [25]

K_2PtCl_4 (1.04 g, 2.5 mmol) was dissolved in 20 mL distilled water, the resulted solution was purged with argon for 20 min, and then $P(n\text{-}Bu)_3$ (1.07g, 5.3 mmol) was injected via a 2-mL injector. Argon was bubbled through the solution for another 20 min, and the mixture was stirred at room temperature for another 3 h under argon atmosphere. After the reaction was finished, the solid was filtrated out and recrystallized from absolute ethyl alcohol to get the white solid (1.20 g, 71%).

^{1}HNMR (400MHz, $CDCl_3$) δ: 2.00 (t, J = 8.0 Hz, 12H), 1.53~1.63 (m, 12H), 1.43~1.49 (m, 12H), 0.95 (t, J = 6.0 Hz, 18H).

Compound (3)

$Pt(PPh_3)_2Cl_2$ (1.50 g, 2.2 mmol) and CuI (39.0 mg, 0.2 mmol) were dissolved in 15 mL triethylamine and 45 mL THF, and then nitrogen was bubbled through the mixture for 20 min and 4-propyl-phenylacetylene (0.27 g, 1.8 mmol) was added. Nitrogen was bubbled for another 20 min and then the mixture was stirred for 3 days under nitrogen atmosphere. After the reaction was finished, the mixture was filtrated to remove the undissolved solid and then the solvent was removed under reduced pressure to obtain the crude product. Purification of the crude product by flash chromatography with petroleum ether/ dichloromethane (2:1) as the eluant provided the product as yellow solid (1.20 g, 75.8%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.16 (d, J = 8.0 Hz, 2H), 7.02 (d, J = 8.0 Hz, 2H), 2.53 (t, J = 8.0 Hz, 2H), 2.10 – 1.92 (m, 12H), 1.69 – 1.51 (m, 14H), 1.51 – 1.37 (m, 12H), 0.93 (t, J = 6.0 Hz, 21H).

Compound (4) [14]

A mixture of 41 g (1.0 mol) acetonitrile, 46 g (1.0 mol) absolute ethanol and 80 mL benzene were treated with hy-

drogen chloride at 20-25 °C until 1.2-1.5 mol had been absorbed (about 2 h). Stirring was continued for 16~20 h. The temperature was controlled below 40 °C to avoid the decomposition of the product into acetamide and ethyl chloride (the process was strongly exothermic). The crystallized product was filtered and dried as quickly as possible under vacuum.

52.0 g of ethyl acetimidate hydrochloride was added quickly at 20-25 °C to the vigorously stirred mixture of 105 mL of methylene dichloride and 86 g of potassium carbonate dissolved in 300 mL of water (slightly endothermic). The organic phase was separated after mixed for 7~ 10 min and the aqueous phase was extracted with 60 mL fresh methylene dichloride. The organic phases were combined and dried with anhydrous potassium carbonate over night in a refrigerator. The dry solution was then concentrated by rapid distillation of the solvent. The residue contained about 80-85% ethyl acetimidate hydrochloride. 3 mL (52.5 mmol) glacial acetic acid was added to the residue gradually during 30 min. The temperature of the resulting mixture was controlled between 25 to 30 °C during this addition process. Then the mixture was stirred 17 h at RT. The solvent was removed, and the residue was diluted with 30 mL of methylene chloride, the solid was removed by filtration. The solvent of the filtrate was then removed. The residue was distilled and the product was collected at 150 - 155 °C with yield 95%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 2.58 (s, 9H)

Compound (5)

To a mixture of $PdCl_2(PPh_3)_2$ (175 mg, 0.3 mmol) and CuI (190 mg, 1.0 mmol) in THF (30 mL), 4-bromobenzaldehyde (1.85 g, 10 mmol), trimethylsilyl acetylene (1.12 mL, 12 mmol), and NEt_3 (10 mL) were added. The resulted mixture was stirred for 24 h at room temperature. The solvent was removed and 30 mL CH_2Cl_2 was added. The mixture was washed with water (3 × 30 mL). The organic phase was dried with $MgSO_4$ and the solvent was removed by rotary evaporation. Purification by column chromatography (Silica gel, CH_2Cl_2/hexane 1:2) gave 4-(2-(trimethylsilyl)ethynyl) -benzaldehyde derivative as white solid (yield 85%).

To a stirred solution of 4-(2-(trimethylsilyl)ethynyl) benzaldehyde (5 mmol) in CH_3OH (30 mL), K_2CO_3 (69 mg, 0.5 mmol) was added. The mixture was stirred for 24 h at room temperature, and the solvent was removed. The residue was diluted with 30 mL Et_2O and washed with water (3 × 30 mL). The organic phase was dried over $MgSO_4$ and the solvent was removed by rotary evaporation. Purification by a flash colum chromatography (Silica gel, Et_2O) provide **5** as white solid (546 mg, yield 84%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.04 (s, 1H), 7.87 (d, J = 8.0, 2H), 7.67 (d, J = 8.0, 2H), 3.32 (s, 1H).

Compound (6)

A three-neck flask assembled with a condenser and a dropping funnel was charged with 0.47 g (3.6 mmol) 4-ethynylbenzaldehyde, 5 mL methanol and 3 mL KOH solution (10%). The resulted mixture was heated to reflux, and then 0.12 g (1 mmol) 2,4,6-tris(methyl)-s-triazine dissolved in 8 mL methanol was dropped into the flask within 4 h. The reaction was refluxed for another 24 h after the addition, then the solid was filtered out and washed by benzene/ethanol (10/1, V/V). Purification by column chromatography (Silica, CH_2Cl_2/Et_2O 1:1) to provide **6** 230 mg. yield: 50%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (d, J = 16 Hz, 3H), 7.65 (d, J = 8.0, 6H), 7.56 (d, J = 8.0, 6H), 7.18 (d, J = 16 Hz, 3H), 3.21 (s, 3H).

Compound (1) Compound **(3)** 1.10 g (1.44 mmol) and CuI 29 mg (0.15 mmol) were dissolved in 10 mL triethylamine and 30 mL THF, and then the mixture was bubbled nitrogen for 20 min. Compound **(6)** 0.18 g (0.4 mmol) was added. The mixture was bubbled nitrogen for another 20 min and stirred for 3 days under nitrogen atmosphere. After the reaction was finished, the undissolved solid was filtrated out and the solvent was removed under reduced pressure to obtain the crude product. Purification by flash chromatography with petroleum ether/dichloromethane (2:1) as the eluant provided the pure produce as yellow solid (0.51 g, 47.8%). Yield: 45%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25 (d, J = 16 Hz, 3H), 7.57 (d, J = 8.0 Hz, 6H), 7.33 (d, J = 8.0 Hz, 6H), 7.22 (d, J = 8.0 Hz, 6H), 7.12 (d, J = 16 Hz, 3H), 7.05 (d, J = 8.0 Hz 6H), 2.56 (t, J = 8.0 Hz , 6H), 2.16 (m, 36H), 1.65 (m, 36H), 1.42 (m, 42H), 0.95 (m, 63H). MS (TOF): m/z =2683.7[M+]. Anal. Calcd. For $C_{138}H_{213}N_3P_6Pt_3$: C, 61.72; H, 8.00; N, 1.56. Found: C, 62.25; H, 8.07; N, 1.54.

CONFLICT OF INTEREST

The author(s) confirm that this article content has no conflicts of interest.

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SUPPLEMENTARY DATA

The detailed experimental processes and character spectra can be found in the supplementary data.

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