

SUPPORTING INFORMATION

Electron donating group stimulated aggregation induced emission enhancement of oligophenylenevinylene-cored luminogens

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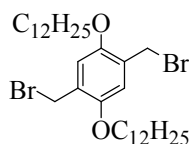
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Experimental

1. General

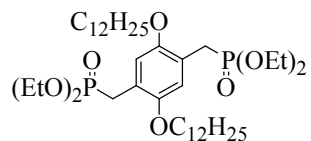
All chemicals were purchased commercially from Sigma-Aldrich and Spectrochem companies and used without further purification. All reactions were carried out under an inert atmosphere in flame dried flasks. After drying, organic extracts were evaporated under reduced pressure and the residue was column chromatographed on silica gel (Spectrochem, particle size 100-200 mesh), using an ethyl acetate–petroleum ether (60-80 °C) mixture as eluent unless specified otherwise. All melting points are uncorrected. ¹H (300 MHz) and ¹³C (75 MHz) NMR spectra were recorded with a Bruker 300 MHz instrument in CDCl₃ and D6-DMSO. Elemental analyses (C, H, and N) were performed with a Perkin–Elmer 240C elemental analyzer. Absorption and fluorescence spectra of all compounds were recorded on a Hitachi U-3510 spectrophotometer and Perkin–Elmer LS55 fluorescence spectrometer at 25 °C.

Synthesis of 1,4-bis(bromomethyl)-2,5-bis(dodecyloxy)benzene (2).¹



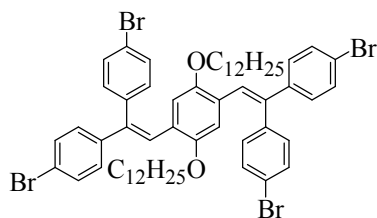
paraformaldehyde (1.01 g, 33.5 mmol), 1,4- bis(dodecyloxy)benzene (5.100 g, 11.20 mmol), HBr (17.5 mL, 50 wt% in acetic acid) and 30.0 mL of acetic acid were placed into a round bottom flask. The mixture was stirred under room temperature for 30 min and 80 °C for 3.0 h. Then the solvents were completely removed under reduced pressure. The crude product was purified by redissolving it in chloroform and reprecipitated out of ethanol to give a white powder (5.66 g, yield 80%). ¹H NMR (300 MHz, CDCl₃) δ 6.84 (s, 2H), 4.52 (s, 4H), 3.98 (t, 4H, *J* = 6.3 Hz), 1.87-1.75 (m, 4H), 1.59-1.42 (m, 4H), 1.42-1.22 (m, 32H), 0.88 (t, 6H, *J* = 6.9 Hz).

Synthesis of Tetraethyl(2,5-Dimethoxy-1,4-phenylene)bis(methylene)diphosphonate (3).²



Compound **2** (19.52 g, 30.86 mmol) and triethyl phosphite (20 mL) were refluxed at 150 °C for 12 h. The excess triethyl phosphite was removed by vacuum distillation, and the white solid was obtained as product. The white solid product was purified by repeated washing with hexane. Yield = 22.01 g (96%). ¹H NMR (300 MHz, CDCl₃) δ 6.91 (s, 2H), 4.09-3.98 (m, 8H), 3.97-3.87 (t, 4H, *J* = 6.6 Hz), 3.22 (d, 4H, *J* = 20.1 Hz), 1.85-1.69 (m, 4H), 1.48-1.39 (m, 4H), 1.20-1.38 (m, 40H), 0.88 (t, 6H, *J* = 6.6 Hz).

Synthesis of 1,4-bis[2,2-bis(4-bromophenyl)vinyl]-2,5-bisdodecyloxybenzene (4).

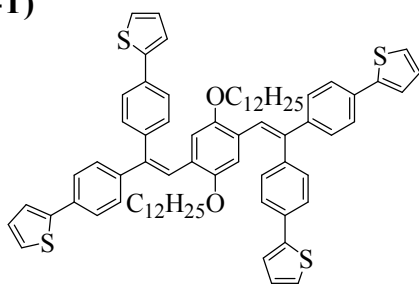


Compound **3** (1.07 g, 1.44 mmol) and 4,4'-dibromobenzophenone (1.08 g, 3.17 mmol) in dry THF (30 mL) and potassium tert-butoxide (8.7 mL, 1 M THF) were added in ice cold condition under nitrogen atmosphere. The reaction mixture was stirred at room temperature for 12 h. It was poured into methanol, and then, precipitate was filtered and dried. Further purification was done by column chromatography (silica gel, ethyl acetate/petroleum ether 1:19). Yield = 1.34 g (83%). Mp 100–101 °C; IR (KBr, cm⁻¹) 2919, 2853, 2345, 1542, 1482; ¹H NMR (300 MHz, CDCl₃) δ 7.48 (d, 4H, *J* = 8.4 Hz), 7.41 (d, 4H, *J* = 8.4 Hz), 7.28 (s, 2H), 7.14 (d, 4H, *J* = 8.4 Hz), 7.08 (d, 4H, *J* = 8.4 Hz), 6.17 (s, 2H), 3.30 (t, 4H, *J* = 7.2 Hz), 1.50-1.21 (m, 40H), 0.88 (t, 6H, *J* = 6.6 Hz); ¹³C NMR (75 MHz, CDCl₃) δ 150.4, 141.6, 139.4, 139.2, 131.9, 131.7, 131.6, 131.1, 130.9, 128.8, 127.9, 127.3, 125.5, 123.2, 121.3, 113.4, 68.5, 31.6, 29.5, 29.4, 29.3, 29.0, 28.9, 26.0, 22.4, 13.8; MALDI-TOF MS *m/z* 1118.65 (M⁺, 80%), 1040.71 (100%). Anal. Calcd for C₅₈H₇₀Br₄O₂: C, 62.27; H, 6.31. Found: C, 62.21; H, 6.22.

General procedure 1- Preparation of tetra-substituted OligoPVs 5/6 using Suzuki coupling reaction

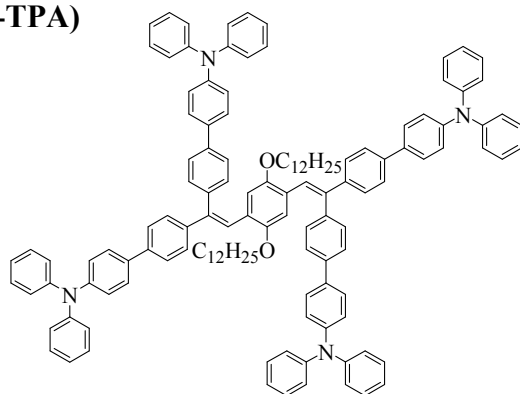
To a solution of compound **4** (1.0 mmol) and boronic acid (4.8 mmol) in toluene (15 mL) was added tricaprylylmethylammoniumchloride (Aliquat[®] 336) (3 drops) and 2 M potassium carbonate aqueous solution (4 mL). The mixture was stirred for 0.5 h. Pd(PPh₃)₄ (0.2 mmol) was added to the reaction mixture and stirred at 90 °C for 16 h. After cooling to room temperature, reaction mixture was poured into water (15 mL) and extracted with ethyl acetate (3 × 10 mL). The combined organic layer was washed with brine (5 mL) and dried over anhydrous Na₂SO₄. Evaporation of solvent and purification by column chromatography (silica gel, ethyl acetate/petroleum ether 1:19) gave the pure products.

Compound **5** (OligoPV-T)



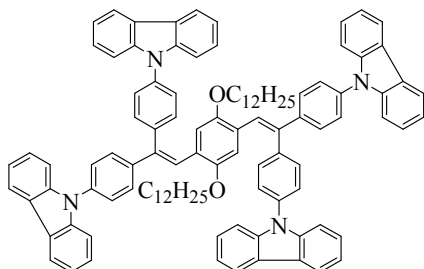
General procedure 1 was followed using compound **4** (100 mg, 0.089 mmol), 2-thienylboronic acid (62.6 mg, 0.429 mmol) and Pd(PPh₃)₄ (23 mg, 0.02 mmol). The crude product was purified using column chromatography (silica gel, ethyl acetate/petroleum ether 1:19) to yield the compound **5** (74 mg, 74%) as a yellow solid. Mp: >200 °C; IR (KBr, cm⁻¹) 2930, 2865, 2341, 1579; ¹H NMR (300 MHz, CDCl₃) δ 7.63 (d, 4H, *J* = 8.1 Hz), 7.55 (d, 4H, *J* = 8.1 Hz), 7.39-7.22 (m, 15H), 7.21 (s, 2H), 7.15-7.03 (m, 5H), 6.32 (s, 2H), 3.28 (t, 4H, *J* = 6.0 Hz), 1.50-1.35 (m, 4H), 1.34-1.09 (m, 36H), 0.87 (t, 6H, *J* = 6.9 Hz); ¹³C NMR (75 MHz, CDCl₃) δ 150.7, 144.2, 144.0, 142.4, 140.7, 140.2, 133.5, 133.4, 132.3, 132.2, 131.5, 131.2, 128.6, 128.4, 128.1, 128.0, 127.7, 126.2, 126.0, 125.6, 124.8, 124.7, 124.3, 123.7, 123.1, 123.0, 122.6, 113.8, 68.8, 31.9, 29.7, 29.6, 29.4, 29.3, 29.2, 25.9, 22.7, 14.1; MALDI-TOF MS *m/z* 1131.90 (M⁺, 80%), 1130.97 (100%). Anal. Calcd for C₇₄H₈₂O₂S₄: C, 78.54; H, 7.30. Found: C, 78.44; H, 7.35.

Compound 6 (OligoPV-TPA)



General procedure 1 was followed using compound **4** (100 mg, 0.089 mmol), 4-(diphenylamino)phenylboronic acid (124 mg, 0.429 mmol) and Pd(PPh₃)₄ (23 mg, 0.02 mmol). The crude product was purified using column chromatography (silica gel, ethyl acetate/petroleum ether 1:19) to yield the compound **6** (112 mg, 71%) as a yellow solid. Mp: >200 °C; IR (KBr, cm⁻¹) 2924, 2858, 2350, 1458; ¹H NMR (300 MHz, CDCl₃) δ 7.59 (d, 4H, *J* = 8.4 Hz), 7.53-7.45 (m, 10H), 7.40 (d, 4H, *J* = 8.4 Hz), 7.34-7.24 (m, 31H), 7.19-7.10 (m, 20H), 7.02-6.92 (m, 5H), 6.32 (s, 2H), 3.28 (t, 4H, *J* = 6.6 Hz), 1.35-1.10 (m, 40H), 0.84 (t, 6H, *J* = 6.3 Hz); ¹³C NMR (75 MHz, CDCl₃) δ 150.7, 147.6, 147.3, 147.1, 141.9, 141.0, 139.6, 139.5, 139.4, 134.5, 131.0, 129.2, 128.0, 127.5, 126.8, 126.2, 124.4, 123.9, 123.8, 123.0, 122.9, 113.7, 68.6, 31.8, 29.6, 29.3, 29.2, 26.0, 22.6, 14.0; MALDI-TOF MS *m/z* 1776.70 (MH⁺, 100%). Anal. Calcd for C₁₃₀H₁₂₆N₄O₂: C, 87.90; H, 7.15; N, 3.15. Found: C, 87.83; H, 7.17; N, 3.28.

Synthesis of compound 7 (OligoPV-C): *Buchwald–Hartwig amination*



A mixture of Compound **4** (100 mg, 0.089 mmol), carbazole (75.3 mg, 0.45 mmol), palladium(II) acetate (23 mg, 0.1 mmol), sodium tert-butoxide (55.7 mg, 0.58 mmol) and

anhydrous toluene (10 mL) were charged in a flame dried flask. The mixture was then degassed by nitrogen purging for 30 min. Tri-*tert*-butylphosphine (71 mg, 0.35 mmol) dissolved in toluene (3 mL) was added *via* syringe. After evacuated and refilled with argon ($\times 5$), the mixture was heated (100°C) for 3 days and then allowed to cool to room temperature. The mixture was diluted with chloroform (100 mL), washed with brine ($\times 2$) and water, dried over anhydrous Na₂SO₄, filtered and concentrated to give a viscous oil, to which was added methanol (20 mL) with stirring. The precipitate was then filtered, rinsed with methanol. The crude product was purified using column chromatography (silica gel, ethyl acetate/petroleum ether 1:19) to yield the compound **7** (64 mg, 49%) as a yellow solid. Mp: 185–187 °C; IR (KBr, cm⁻¹) 2921, 2851, 2361, 1508; ¹H NMR (300 MHz, CDCl₃) δ 7.71 (d, 4H, $J = 8.4$ Hz), 7.65 (d, 4H, $J = 8.4$ Hz), 7.63-7.17 (m, 42H), 6.26 (s, 2H), 3.37 (t, 4H, $J = 5.7$ Hz), 1.56-1.13 (m, 40H), 0.85 (t, 6H, $J = 6.6$ Hz); ¹³C NMR (75 MHz, CDCl₃) δ 150.2, 140.3, 140.2, 137.0, 135.9, 132.4, 132.0, 131.1, 130.2, 129.4, 129.1, 128.2, 128.0, 127.4, 126.5, 126.0, 125.9, 125.1, 125.0, 113.7, 68.8, 31.9, 29.6, 29.3, 29.1, 26.1, 22.6, 14.1; MALDI-TOF MS m/z 1465.33 (MH⁺, 80%), 1466.33 (MH⁺+1, 90%), 1467.33 (MH⁺+2, 100%). Anal. Calcd for C₁₀₆H₁₀₂N₄O₂: C, 86.96; H, 7.02; N, 3.83. Found: C, 86.81; H, 7.09; N, 3.90.

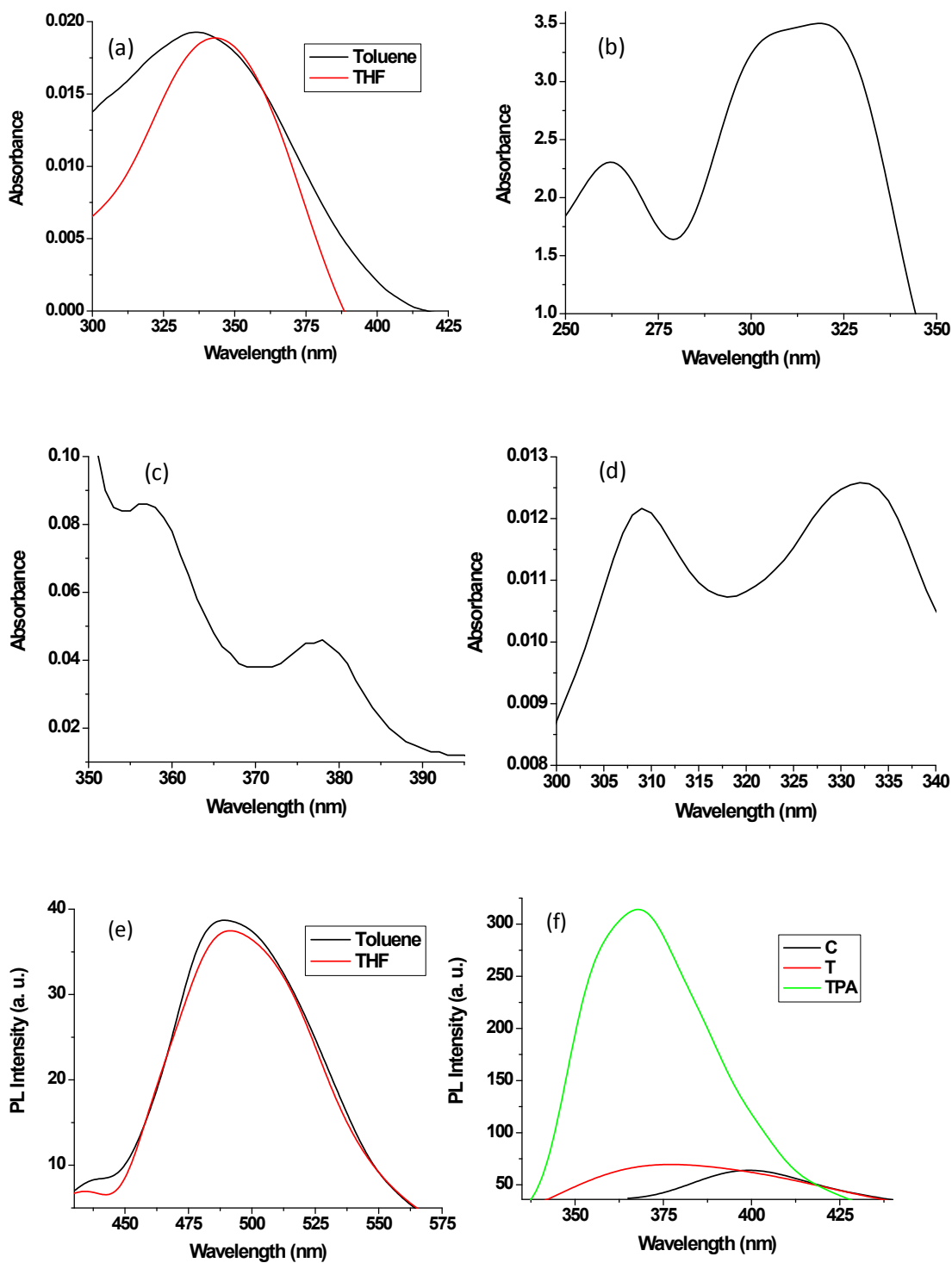


Fig. S1 (a) Absorption spectra of OligoPV-4Br ($C = 1 \times 10^{-6}$ M) in THF. (b), (c) and (d) are the absorption spectra of TPA, C and T respectively ($C = 1 \times 10^{-3}$ M) in THF. (e) Photoluminescence spectra of OligoPV-4Br ($C = 1 \times 10^{-7}$ M) in toluene and THF. (f) Photoluminescence spectra of TPA, C and T ($C = 1 \times 10^{-5}$ M) in THF.

Table 1

Compound	UV-vis (λ_{abs} , nm)	$\epsilon_{\text{max}}/\text{mol}^{-1}\text{cm}^{-1}$	PL	
			λ_{max} , nm	fluorescence intensity amplification factor
TPA	262, 318	3493	368	27.3($I_{\text{OligoPV-TPA}}/I_{\text{TPA}}$)
C	356, 377	86	400	115.3($I_{\text{OligoPV-C}}/I_{\text{C}}$)

ACQ luminophores TPA, C and T without OligoPV -core unit have very low fluorescence intensity and did not show any AIE activity. Fluorescence intensity enhanced enormously when attached with OligoPV -core (27 to 115-fold).

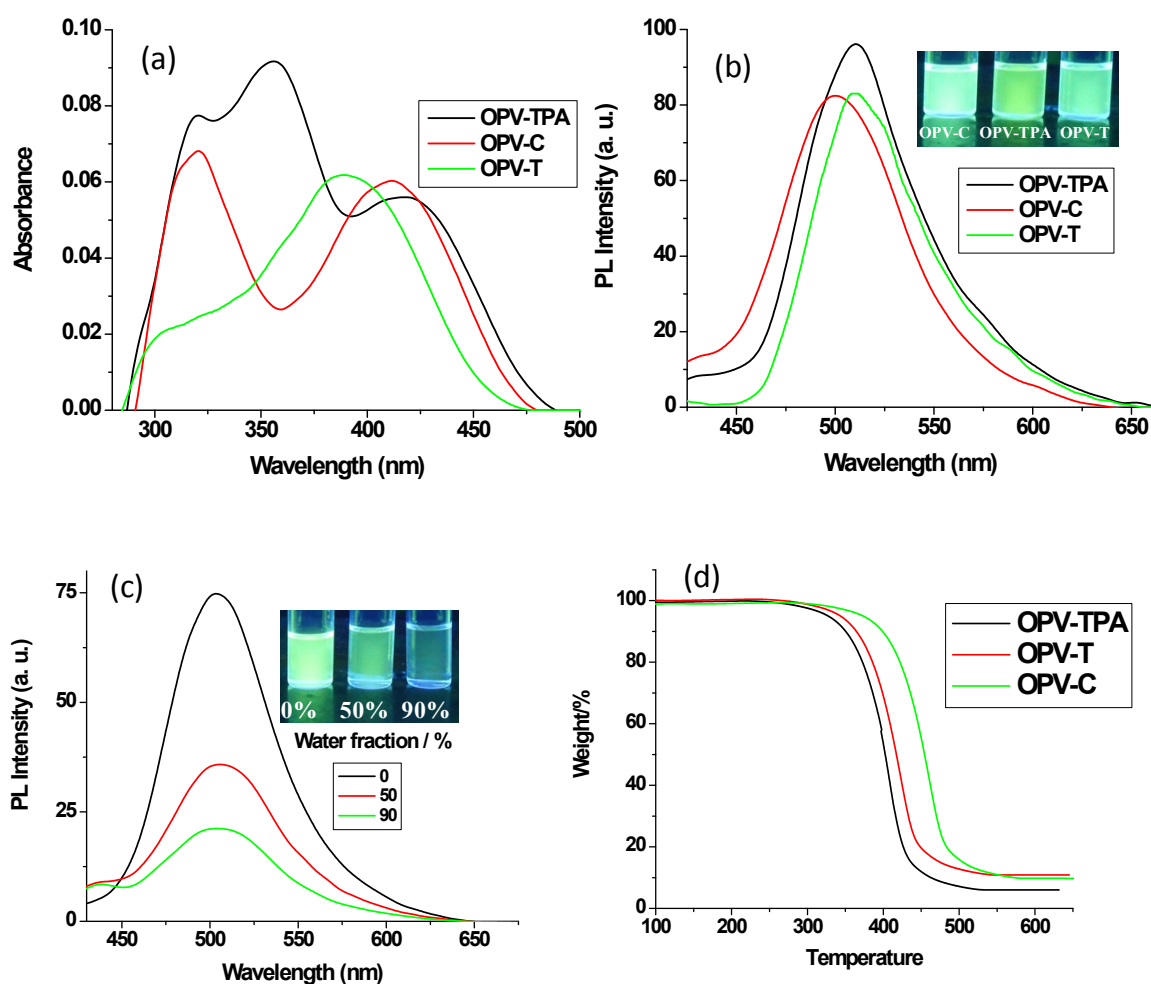


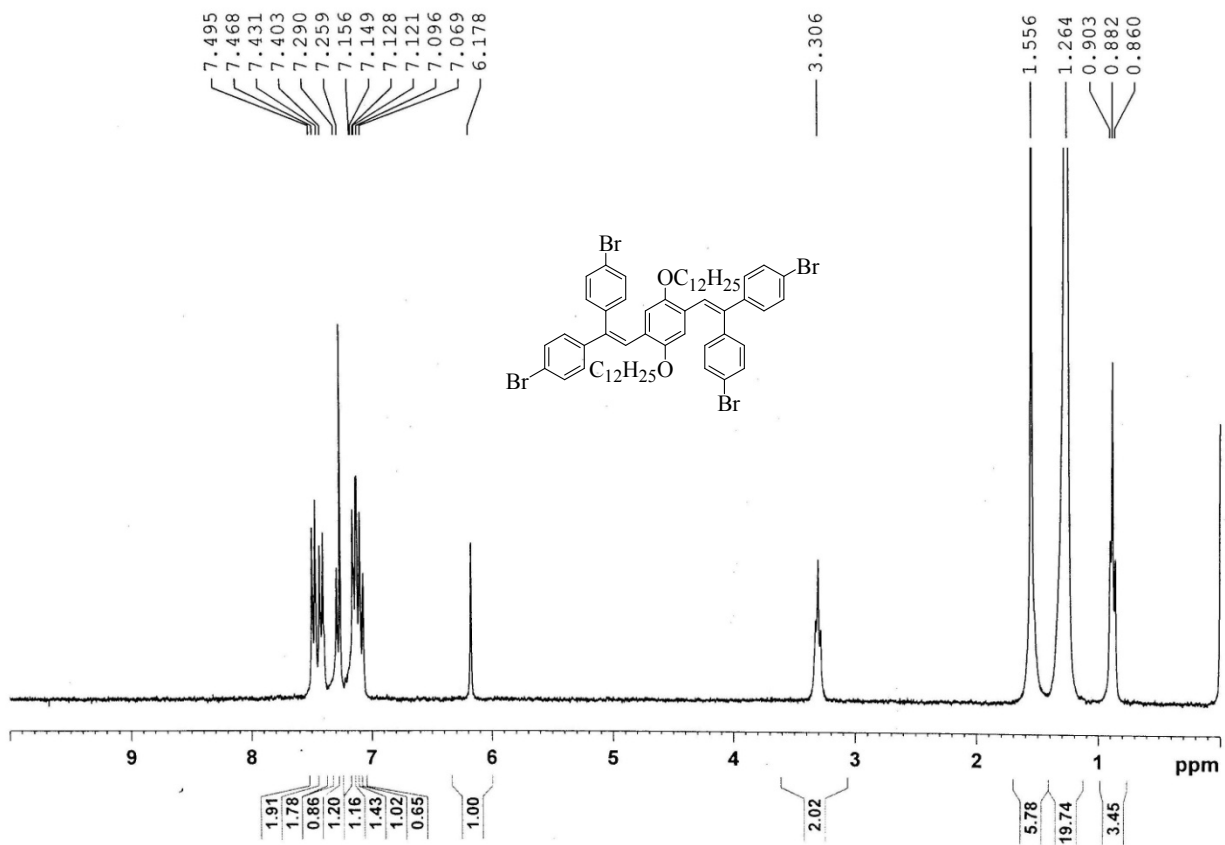
Fig. S2 (a) absorption spectra of OligoPV-cored luminogens ($C = 1 \times 10^{-6}$ M) in toluene. (b) photoluminescence spectra of OligoPV-cored luminogens ($C = 1 \times 10^{-7}$ M) in toluene. Inset: Fluorescence emission image in toluene. (c) Corresponding emission spectra of compound OligoPV-C in aqueous THF with different water-THF ratios at 10^{-6}

⁷ M. Inset: Fluorescence emission image of OligoPV-C (fw = 0, 50 and 90%). (d) TGA curve of luminogens. All photos are taken under UV illumination. Excitation wavelength: 365 nm.

References

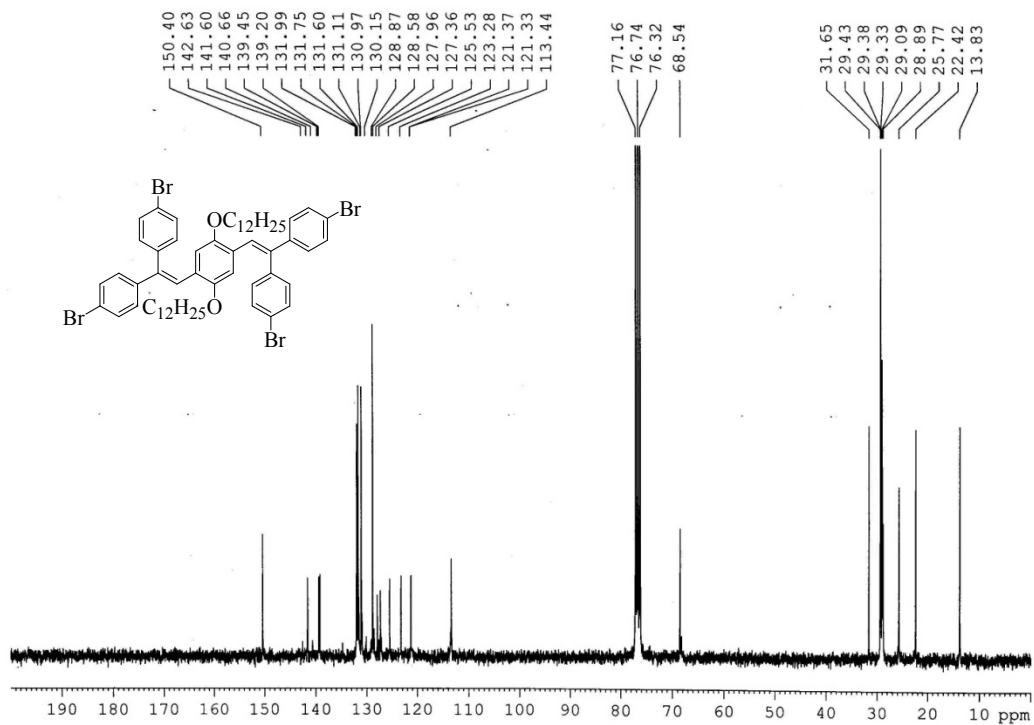
1. B. C. Thompson, Y. -G. Kim, T. D. McCarley, J. R. Reynolds, *J. Am. Chem. Soc.*, 2006, **128**, 12714.
2. D. Jana, B. K. Ghorai, *Tetrahedron Lett.*, 2014, doi: <http://dx.doi.org/10.1016/j.tetlet.2014.07.099>

¹H NMR spectrum of 4



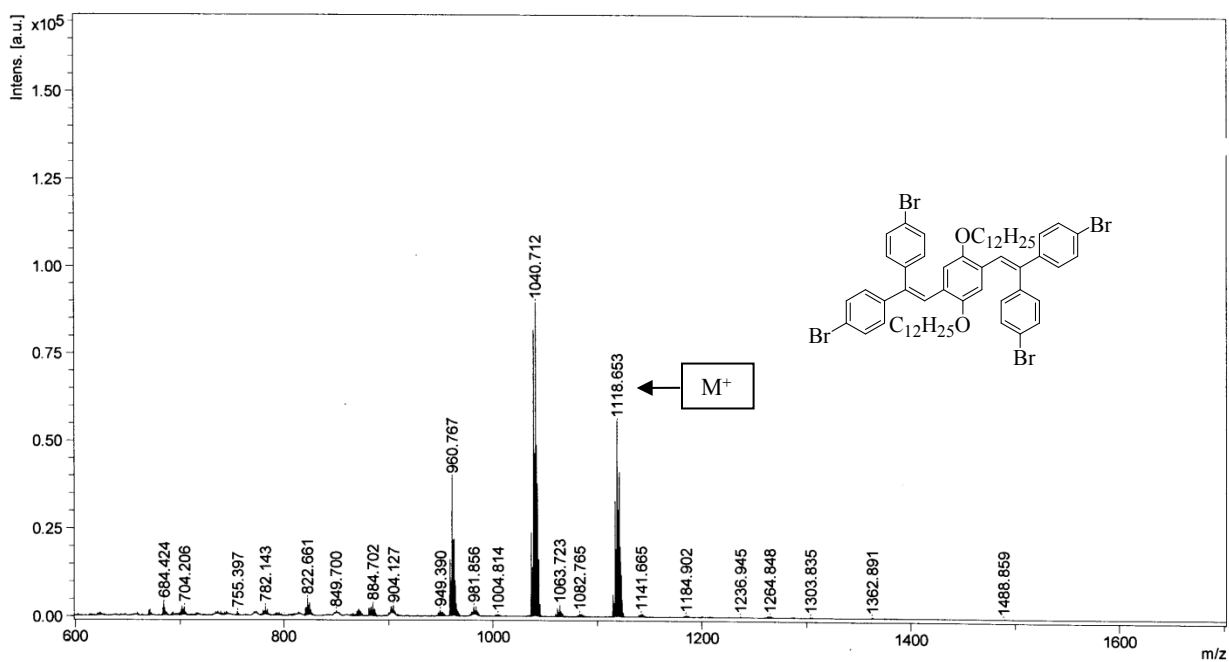
¹³C NMR spectrum of 4

300 MHz NMR Machine; Department of Chemistry; University of Calcutta; SAP-CAS Program
Sample: AP-PR-83R; 13C; CDCL3; Supervisor: Prof. A. Pramanik; Dt: 04/11/14



MALDI-TOF MS of compound 4

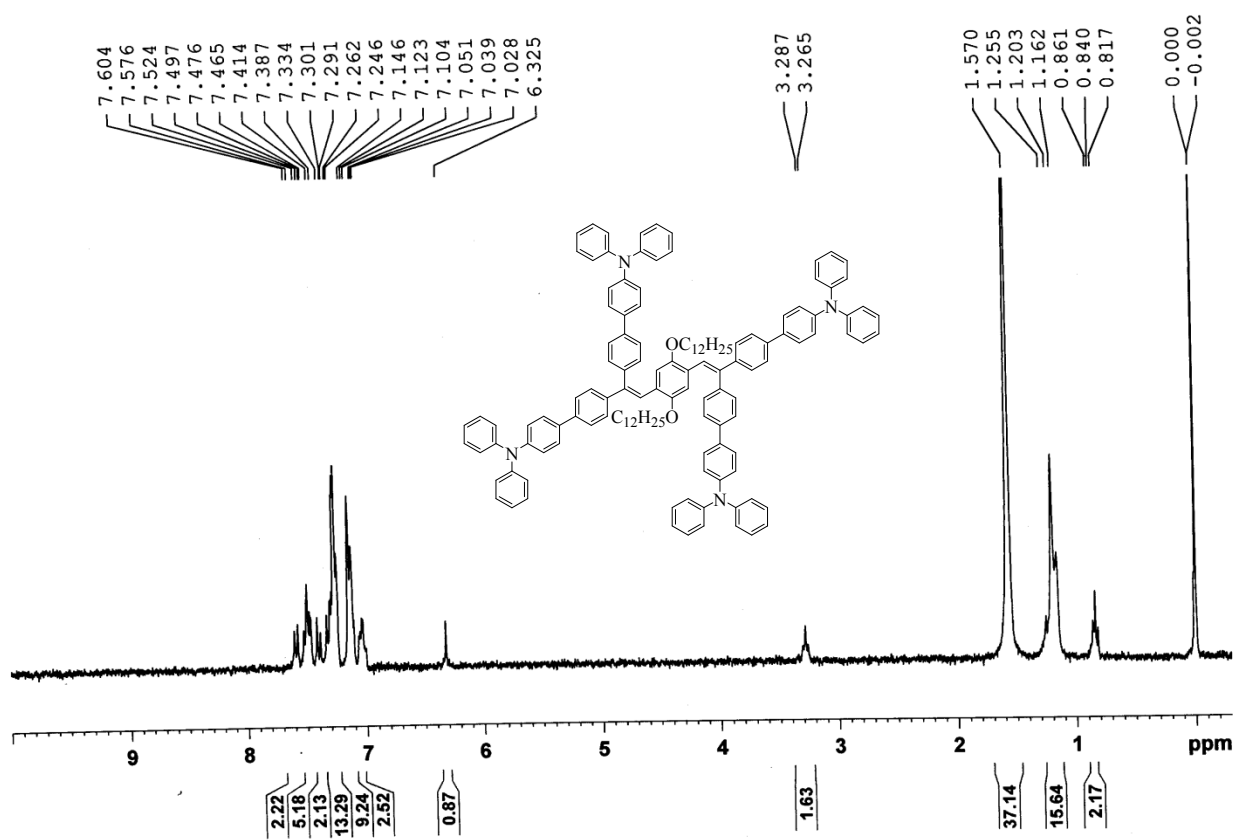
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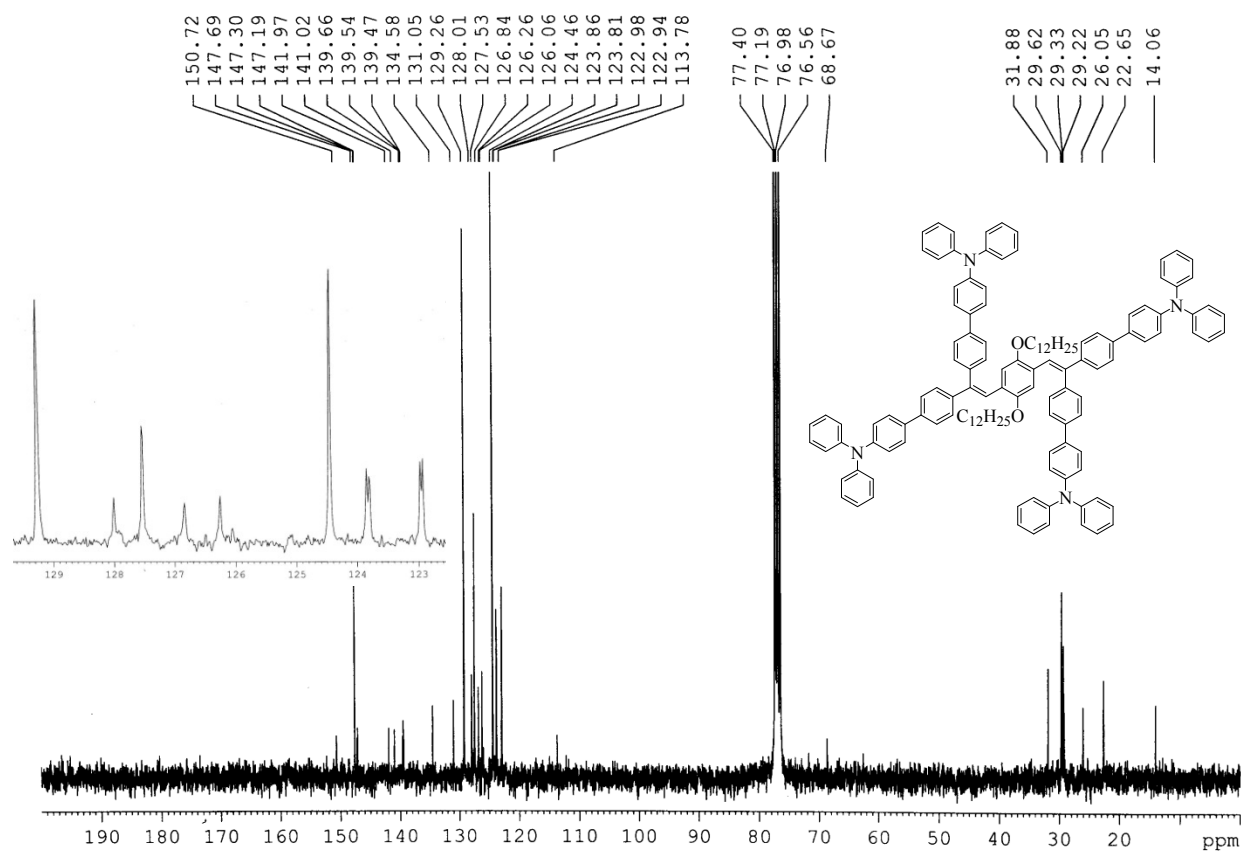
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¹H NMR spectrum of OligoPV-TPA

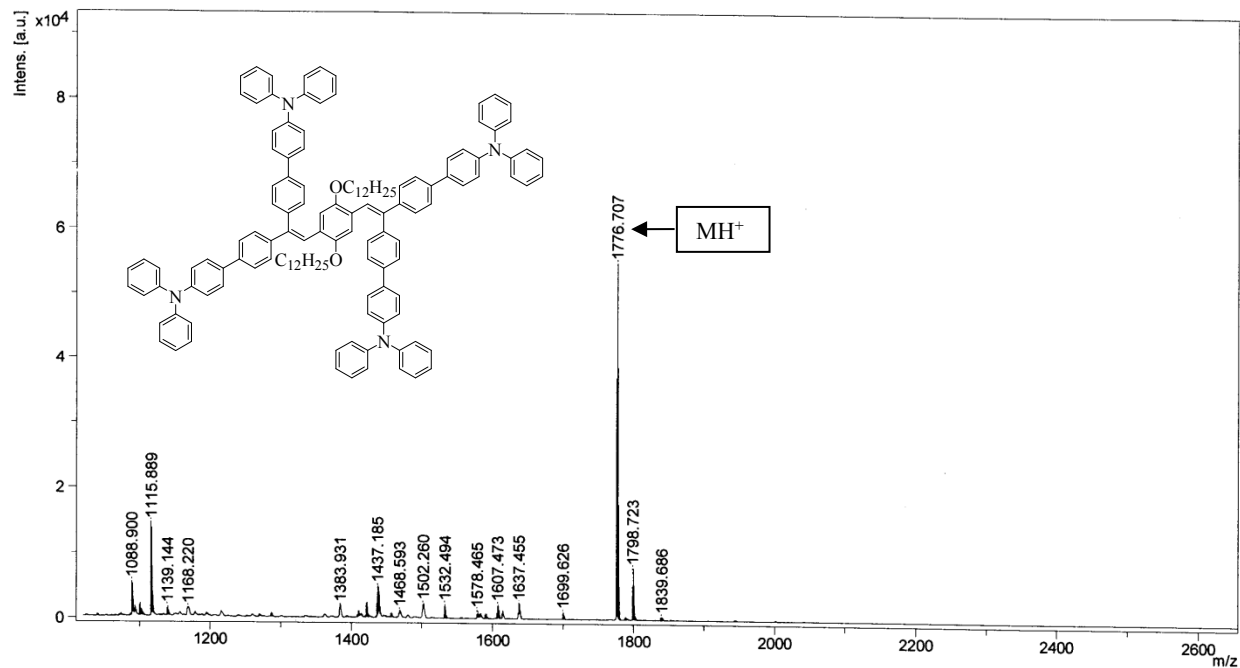


¹³C NMR spectrum of OligoPV-TPA



MALDI-TOF MS of compound **OligoPV-TPA**

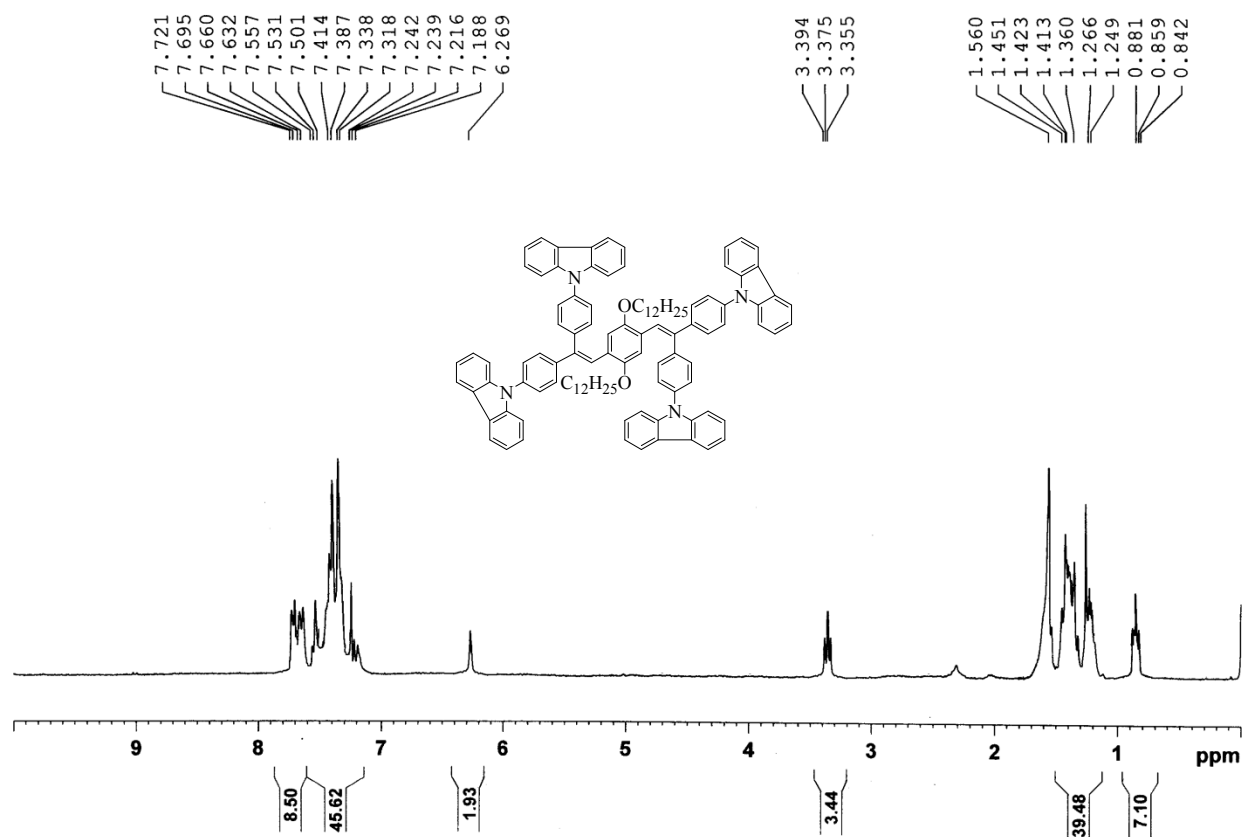
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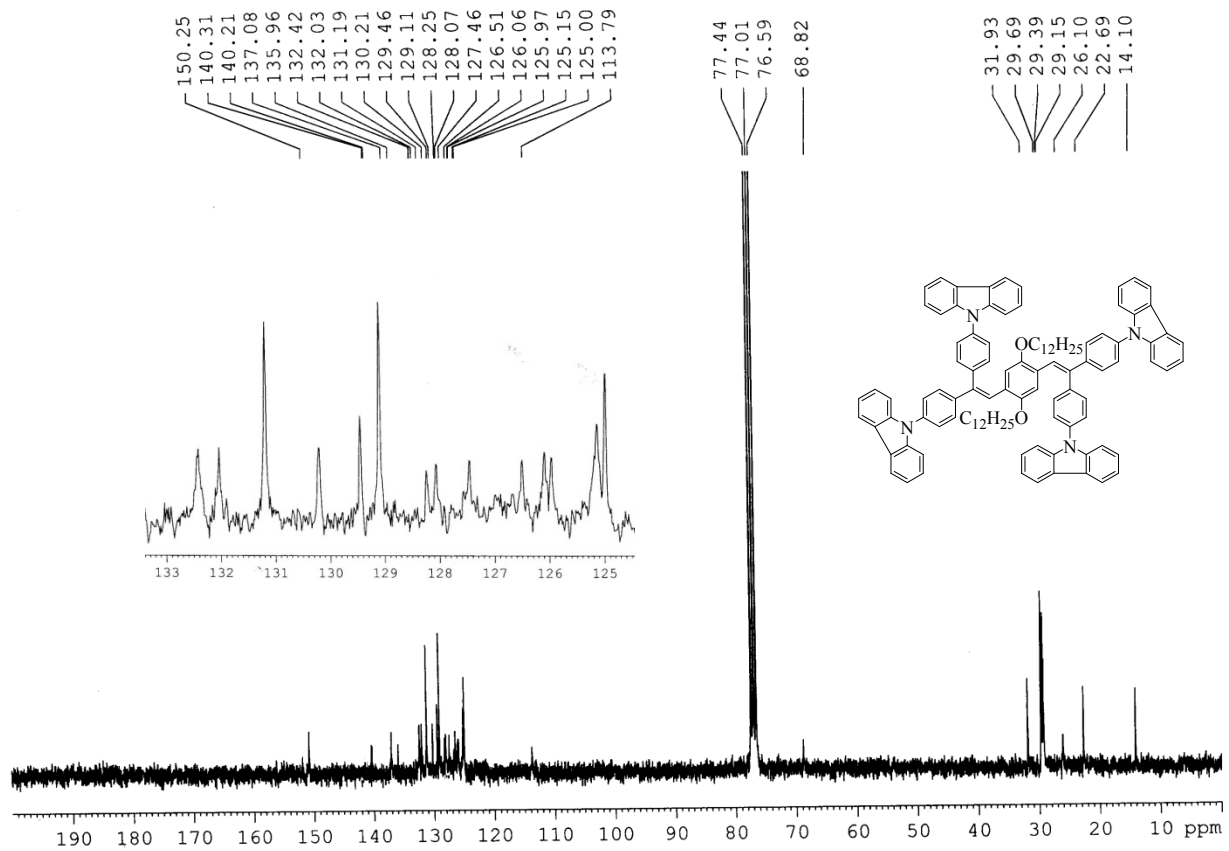
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¹H NMR spectrum of OligoPV-C

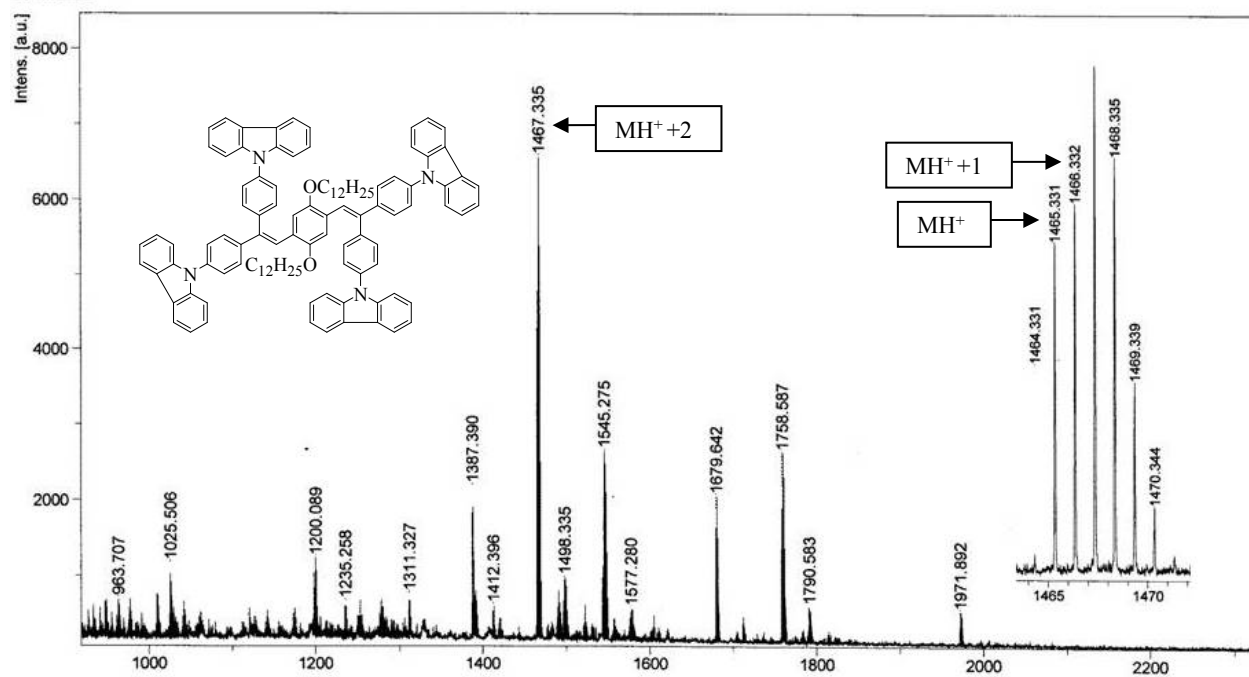


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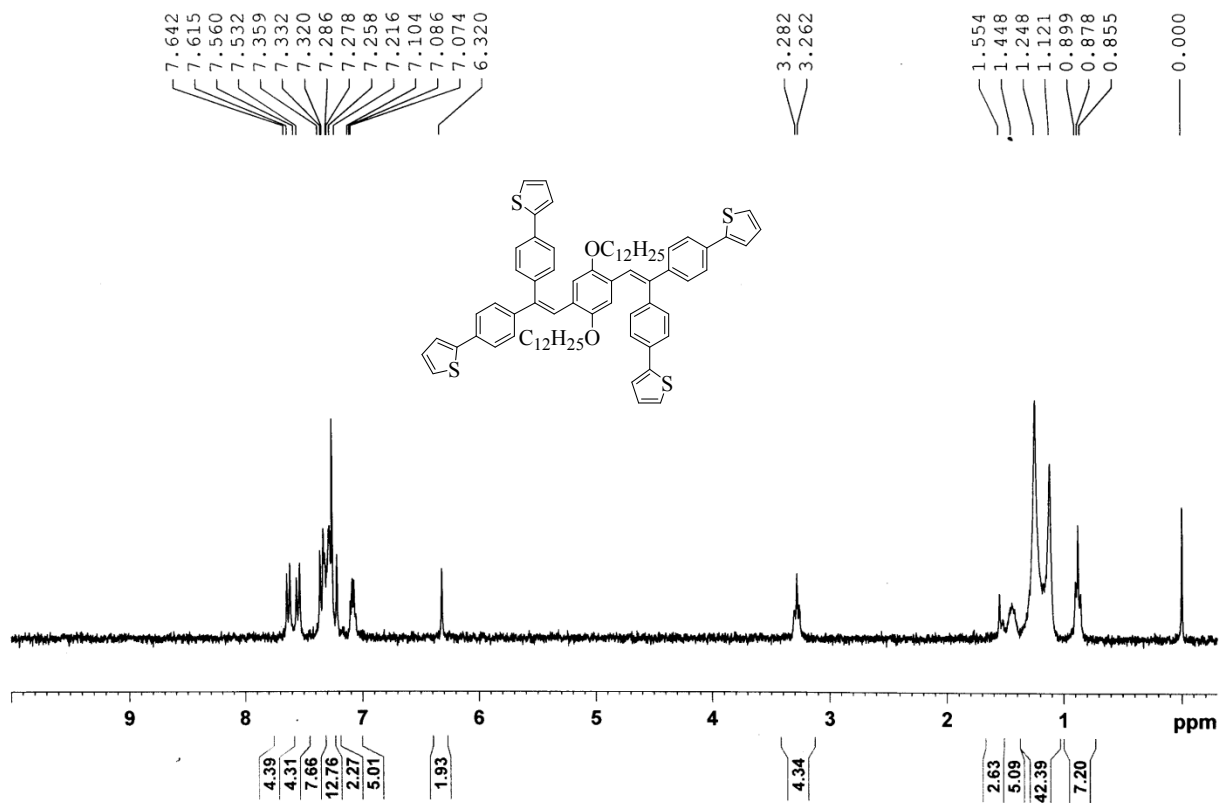


MALDI-TOF MS of compound **OligoPV-C**

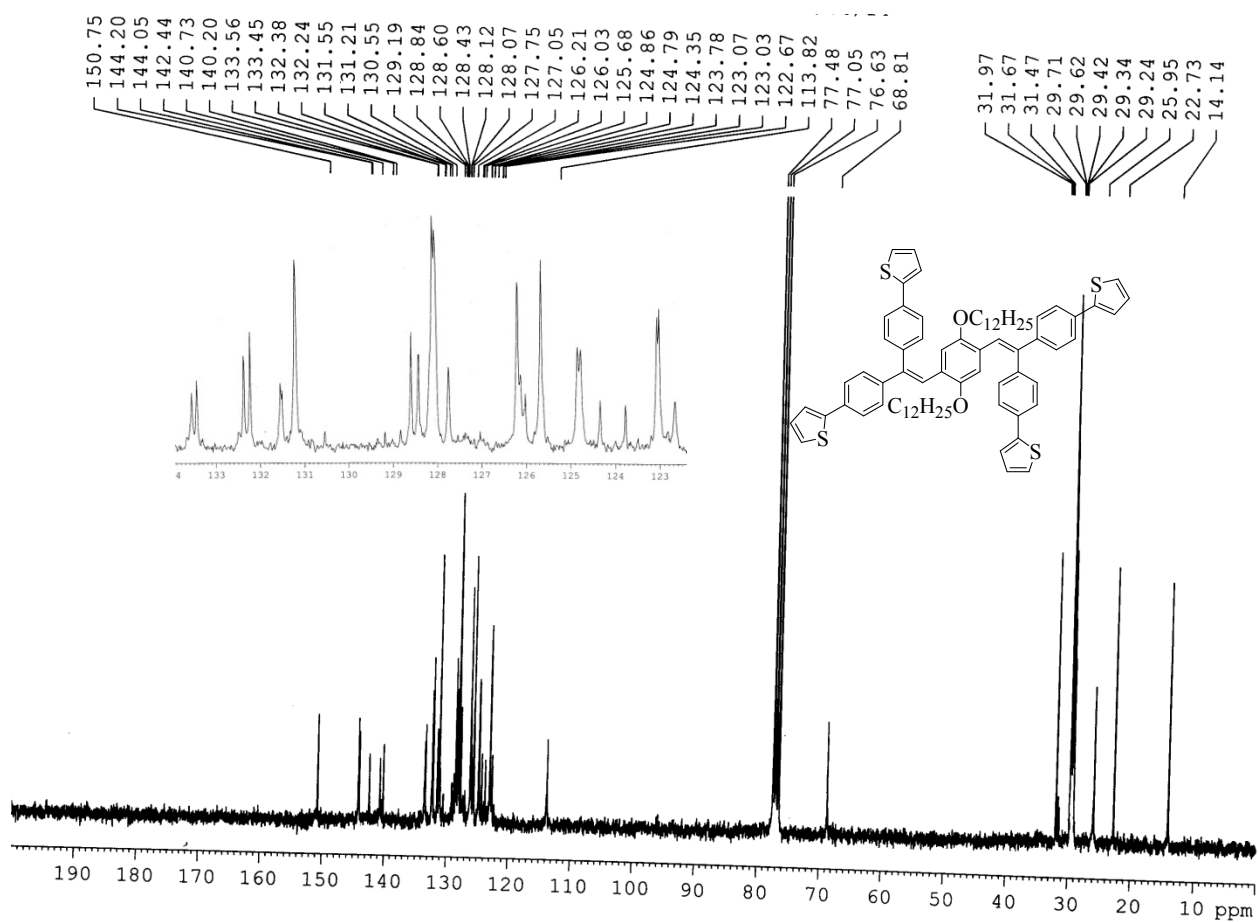
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Comment 2



¹H NMR spectrum of OligoPV-T

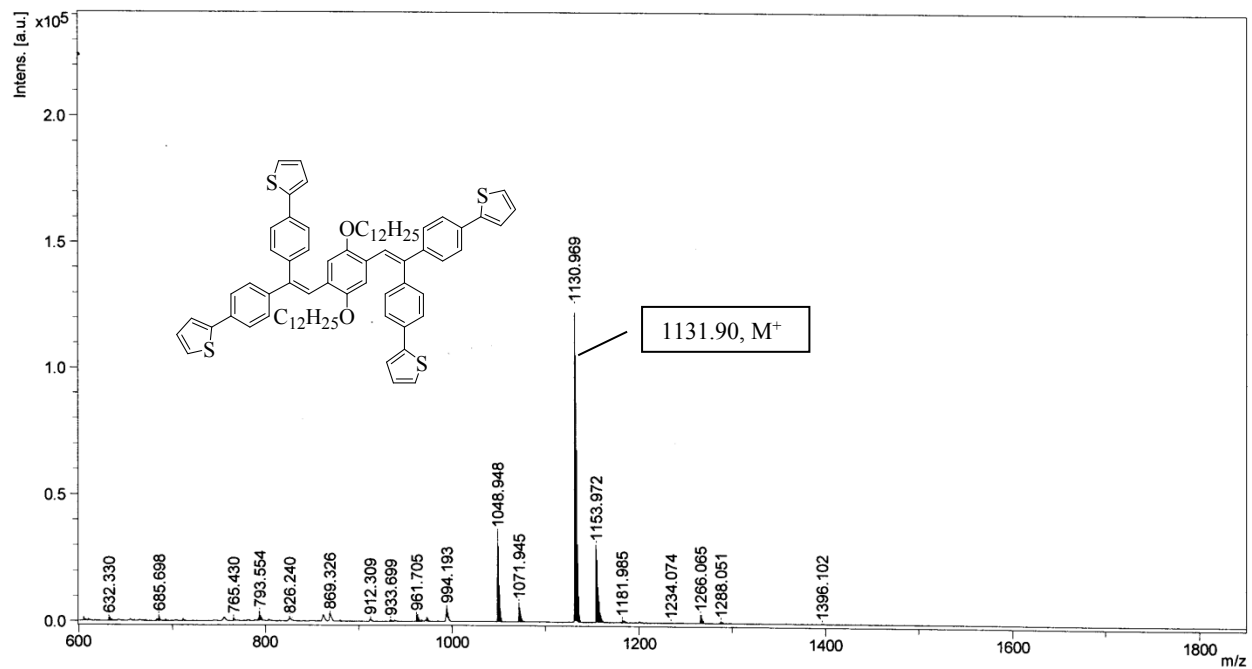


¹³C NMR spectrum of OligoPV-T



MALDI-TOF MS of compound **OligoPV-T**

Comment 1
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