Synthesis of Stilbenes Using Various Catalysts and Investigation of Their Optical Properties

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ABSTRACT: Stilbenes substituted with –CN, –OMe and –Br were synthesized using four different Lewis acid catalysts and their reaction efficiencies were compared. In addition to the McMurry reagents known in literature, a more economical catalyst, ZnCl\textsubscript{2}, was used for the first time in our reaction procedures. Furthermore, bromine substituted stilbenes were subjected to Suzuki coupling reactions to append a triphenylamine (TPA) unit to enhance fluorescence emissions. Solvatochromic properties of synthesized stilbenes were investigated and aggregation caused quenching (ACQ) properties of TPA containing molecules were systematically examined. Structural and optical properties of the stilbenes under study were also theoretically investigated by way of DFT calculations and the experimental results were supported by the computational methods.

1. Introduction

Stilbenes are characterized by two aromatic rings, linked by an ethylene bridge. Their $\pi$-conjugated structures and $E/Z$ isomers exhibit excellent photophysical and photochemical properties.\textsuperscript{1–5} Stilbene compounds are abundant in nature and act as defense compounds in some plants for pathogen attacks. Moreover, their antioxidant,\textsuperscript{6} anti-inflammatory\textsuperscript{7} and anticancer activities,\textsuperscript{7,8} have been of great interest
to scientists. Apart from biological features, their interactions with radiation provide various applications in nonlinear optics, light emitting diodes, and optical brighteners (Scheme 1).

The use of stilbenes for light emitting diodes and optical brighteners has led to tremendous innovation in display technology. Stilbenes, with their luminophore characteristics, may experience two effects in aggregate state; aggregation caused quenching (ACQ) and aggregation induced emission (AIE). ACQ describes the weakened emission of luminophores in solid state when compared to solution.

Scheme 1. Structures of E/Z isomers of some stilbene compounds.

Unlike AIEgens, ACQ-active compounds decay radiatively and shine brighter when they are separated. This trend is observed due to compact packing and strong π-π stacking interactions in ACQ luminophores, leading to undesirable quenching effects in emission. Triphenylamine (TPA) known for its electron donating and efficient charge transport abilities is used in some AIEgens to enhance exciton combination, charge transport and emission. Furthermore, due to its charge transport ability, TPA is commonly used as a donor in donor-acceptor (D–A) systems, to create a low energy charge-transfer (CT) transition.

π-conjugated compounds with D–A type structures have been of great importance due to their efficient use in fluorescent sensors, biological imaging, photovoltaic cells and other optoelectronic applications. Substituted stilbenes are utilized to improve charge transfer characteristics in D–π–A systems.
(Scheme 2); moreover, TPA units incorporated to stilbenes cause bathochromic shifts. Furthermore, presence of strong acceptor units results in marked conjugation, thus, solvatochromic properties.\textsuperscript{22} Solvatochromic properties of organic molecules is well-known, whereby, their emission and absorption bands are largely influenced by solvents with different polarities.\textsuperscript{23–27}

\begin{center}
\includegraphics[width=0.8\textwidth]{scheme2.png}
\end{center}

**Scheme 2.** Possible D-A structures of stilbene compounds.

Stilbene derivatives can be synthesized \textit{via} eight different reaction types: Aldol-type condensation, Siegrist method, Wittig–Horner reaction, Heck reaction, Negishi–Stille reaction, Barton–Kellogg–Staudinger reaction, McMurry reaction and Perkin reaction.\textsuperscript{28} In the McMurry reaction, two aldehydes or ketones are coupled to form an alkene by using a reducing agent, Zn and titanium (IV) chloride. The low valent Ti-induced (TiCl\textsubscript{2}) reductive deoxygenation of carbonyls to olefins takes place in two steps: 1) reductive dimerization of the starting ketones to form a carbon–carbon bond and, 2) deoxygenation of the 1,2-diolate intermediate to give an alkene (Scheme 3).\textsuperscript{29,30} As represented in Scheme 3, Zn is used in multiple steps of the McMurry coupling, therefore, excess amounts are used in reaction procedures. The stereoselectivity of olefin formation depends strongly on the steric bulk of the alkyl groups on the ketone. While McMurry reactions with bulky -R groups mainly lead to $E$ isomers, surprisingly it was found that the $Z$ isomer is the major product of McMurry coupling of acetophenones.\textsuperscript{31–34} In this study, we chose to use McMurry coupling to produce our target stilbenes (Scheme 4). Herein, our main aim was proposing an environmentally friendly synthesis procedure for the targeted stilbene compounds and also understanding their photophysical properties which are important for their applications such as display technology.
Although TiCl₄ is the first proposed catalyst in McMurry olefination procedures, other catalysts such as AlCl₃, SnCl₄ and InCl₃ are also used to develop new synthesis procedures for McMurry coupling mechanism of carbonyl compounds to olefins. In this study, in addition to AlCl₃, SnCl₄ and TiCl₄, we proposed a new McMurry reagent, ZnCl₂.

![Mechanism of McMurry coupling reaction](image)

**Scheme 3.** Mechanism of McMurry coupling reaction.

Thus, we performed olefination mechanism with four different reagents and observed varying performances with each catalyst. After the successful synthesis of seven stilbene molecules (Scheme 4, Table 1), solvatochromic effects on optical properties of 1-5, 7 and 8 were studied. Stilbenes 3 and 4 were synthesized as precursors to 7 and 8. Molecule 6 could not be isolated.

![Synthesis of stilbene derivatives](image)

**Scheme 4.** Synthesis of stilbene derivatives 1–8.
In addition to solvatochromism study, we estimated the possible ACQ effect of DPA donor moiety in compounds 7 and 8. The dependency of luminescence on decreased solubility was measured experimentally and the ACQ effect of DPA moiety on synthesized stilbene compounds was observed.

Besides new synthesis procedures and photophysical measurements, we further investigated the geometrical and photophysical properties of synthesized stilbene compounds computationally. As mentioned previously, stilbenes can exist in two different geometries which are E and Z isomers. Our computational study presents both the geometry analyses of these two isomers to theoretically foresee the energetically favorable isomer and also their expected excited state properties. As expected from different structural orientations, two possible isomers exhibit different excited state properties, thus, they lead to various absorption bands in different strengths. Theoretical analysis of spectra properties were performed with the help of nature of excited states analysis and the investigation of frontier molecular orbital distributions. To conclude, following the experimental synthesis and photophysical property analyses, a computational study was performed to support the understanding of photophysical properties generated from experimental measurements.

2. Experimental Synthesis

Measurements and Material

Reagents and reactants like zinc, zinc chloride, tin tetrachloride, titanium tetrachloride, aluminium chloride, sodium sulfate, sodium hydrogen carbonate, potassium carbonate, tetrakis-(triphenylphosphine) palladium (0) (Pd(PPh3)4), 4-(2-bromoacetyl)benzonitrile, 2-bromo-1-(4-methoxyphenyl)ethanone, 2-bromo-1-(4-bromophenyl)ethanone, were used as received from commercial sources. N,N-Diphenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)anilin was
synthesized according to the published procedure. $^1$H and $^{13}$C NMR spectra were recorded on a Varian model NMR spectrometer (500 MHz). Chemical shifts were reported in ppm downfield from tetramethylsilane for proton and carbon. Fluorescence spectra were obtained using a HITACHI F-4500 fluorescence spectrophotometer. UV-Vis absorption spectra were obtained using a HITACHI U-0080D spectrophotometer.

2.2. Synthesis

4,4'-(but-2-ene-2,3-diyl)dibenzonitrile (1): Zinc (1.75 g, 26.7 mmol) was dissolved in dry THF (30 mL) under N$_2$ atm. The reaction was stirred in an ice bath for 30 min and SnCl$_4$ (3.12 mL, 26.7 mmol) was added dropwise to the reaction mixture. The reaction was heated up to 75 °C and refluxed for 2 h. Then, the reaction mixture was cooled down to room temperature and 4-(2-bromoacetyl)benzonitrile (2 g, 8.9 mmol) dissolved in THF (10 mL) was added to the reaction mixture. The reaction was refluxed overnight under N$_2$ atm. The reaction mixture was filtered and extracted with 500 mL of DCM/water (1:1, v/v) mixture 2 times and with DCM/saturated aqueous solution of NaHCO$_3$ (1:1, v/v) mixture 2 times. The organic layer was dried over Na$_2$SO$_4$ and the solvent was evaporated under atmospheric pressure. The product was purified by column chromatography over silica gel using Hexane/DCM (3:1) as eluent to give white solid product with 49.40% yield (0.667 g). Product 1 was also prepared with ZnCl$_2$. After zinc dissolved in THF was stirred for 30 min in an ice bath, ZnCl$_2$ (3.64 g, 26.7 mmol) was added into the reaction mixture. The mixture was refluxed for 2 h and 4-(2-bromoacetyl)benzonitrile (2 g, 8.9 mmol) dissolved in THF (10 mL) was added dropwise. After 6 h reflux, the reaction mixture was filtered and THF was evaporated in a fume hood. The purification process is same with the method with SnCl$_4$. The reaction with ZnCl$_2$ catalyst gives white solid product with 36.20% yield (0.489 g). Product 1 was also prepared with TiCl$_4$. After zinc dissolved in THF was stirred for 30
min in an ice bath, TiCl₄ (1.688 g, 8.900 mmol) was added into the reaction mixture. The mixture was refluxed for 2 h and 4-(2-bromoacetyl)benzonitrile (1 g, 4.5 mmol) dissolved in THF (10 mL) was added dropwise. After 6 h reflux, the reaction mixture was filtered and THF was evaporated in a fume hood. The purification process is same with the method with SnCl₄. The reaction with TiCl₄ catalyst gives white solid product with 53.50% yield (0.722 g)¹H NMR (500 MHz, CdCl₃) δ 8.03 (d, J = 8.15 Hz, 4H), 7.76 (d, J = 8.20 Hz, 4H), 2.64 (s, 6H) ¹³C NMR (126 MHz, CdCl₃) δ 196.54, 139.90, 132.50, 128.68, 117.91, 116.36,26.76. IR ν/ cm⁻¹: 2217.35 (CN stretching), 1671.50 nm (alkene stretching), Rₚ: 0.25 mp : 63.8 °C, MS (m/z) : [M+1]⁺ calcd for C₁₈H₁₄N₂, 258.32; found 259.2.

4,4'-(but-2-ene-2,3-diyl)bis(methoxybenzene) (2): Zinc (1.71 g, 26.29 mmol) was dissolved in dry THF (30 mL) under N₂ atm. The reaction mixture was stirred for 30 min in an ice bath. After that, SnCl₄ (3.05 mL, 26.19 mmol) was added dropwise. Then, the reaction was refluxed for 2 h and 2-bromo-1-(4-methoxyphenyl)ethanone (2 g, 8.73 mmol) dissolved in THF (10 mL) was added to the reaction mixture at room temperature. The reaction was stirred overnight under N₂ atm at 75 °C. After that, the reaction mixture was filtered and THF was removed in a fume hood. The product was extracted with 500 mL DCM/water (1:1, v/v) mixture 2 times and with 500 mL DCM/saturated aqueous solution of NaHCO₃ (1:1, v/v) 3 times. The product was purified by column chromatography over silica gel using n-Hexane/DCM (3:1, v/v) to give green oily product with 28.46% yield (0.7254 g). Product 2 was also synthesized with TiCl₄ and ZnCl₂ (mass of α-bromo ketone is 1g (4.365 mmol) with 1.189 ZnCl₂ and 1.656 TiCl₄) giving the yields 35.60 % (0.907 g) and 18.30 % (0.466 g) respectively. ¹H NMR (500 MHz, CdCl₃) δ 7.94 (d, J = 8.8 Hz, 4H), 6.93 (d, J = 8.8 Hz, 4H), 3.86 (s, 6H), 2.54 (s, 6H). ¹³C NMR (126 MHz, CdCl₃) δ 196.77,
163.46, 130.56, 130.30, 113.66, 55.43, 26.31. IR ν/ cm−1: 1160.67 (O-C stretching), 1667.87 (alkene stretching), Rf: 0.29, MS (m/z): [M+1]+ calcd for C₁₈H₂₀O₂, 268.35; found 269.13.

4,4′-(but-2-ene-2,3-diyl)bis(bromobenzene) (3): Zinc (1.41 g, 21.58 mmol) was dissolved in dry THF (30 mL) and stirred in an ice bath for 30 min under N₂ atm. Then, SnCl₄ (2.52 mL, 21.58 mmol) was added to the reaction mixture dropwise. After the addition of SnCl₄, the mixture was refluxed for 2 h. Then, 2-bromo-1-(4-bromophenyl)ethanone (2 g, 7.20 mmol) dissolved in 10 mL THF was added to the reaction mixture dropwise at room temperature. The reaction was refluxed overnight under N₂ atm. In the next day, mixture was filtered and THF was removed in a fume hood. The product was extracted with 600 mL DCM/water (1:1, v/v) mixture 3 times and with 600 mL DCM/saturated aqueous solution of NaHCO₃ (1:1, v/v) 3 times. The product was purified by column chromatography over silica gel by using n-Hexane/DCM (5:1, v/v) to give pale yellow solid product with 75% yield (1.93 g). Product 3 was also synthesized with TiCl₄ and ZnCl₂ catalysts (1 g, 3.600 mmol ketone with 4 equivalent zinc (0.941 g) and 2 equivalent lewis acid (0.981 g ZnCl₂, 1.365 g TiCl₄) and gave 71.50 % (1.840 g) and 54.70 % (1.408 g) reaction yields respectively. ¹H NMR (500 MHz, CdCl₃) δ 7.81 (d, J = 8.65 Hz, 4H), 7.59 (d, J = 8.65 Hz, 4H), 2.57 (s, 6H). IR ν/ cm−1: 1667.87 nm, Rf: 0.50 mp: 54.6 °C, MS (m/z): [M+1]+ calcd for C₁₆H₁₄Br₂, 366.09; found 363.16.

4-(3-(4-bromophenyl)but-2-en-2-yl)benzonitrile (4): Zinc (1.75 g, 26.77 mmol) was dissolved in dry THF (30 mL) and stirred in an ice bath for 30 min under N₂ atm. After 30 min, SnCl₄ (3.12 mL, 26.77 mmol) was added dropwise and the reaction mixture was refluxed for 2 h. After 2 h, reaction was cooled down to room temperature and the mixture of 2-bromo-1-(4-bromophenyl)ethanone (1.02 g, 4.46 mmol) and 4-(2-bromoacetyl)benzonitrile (1 g, 4.46 mmol) dissolved in 15 mL was added to the reaction mixture. The reaction was refluxed overnight under
N₂ atm. The mixture was filtered and THF was removed in a fume hood. Then, the mixture was extracted with 500 mL DCM/water (1:1, v/v) mixture 3 times and with 500 mL DCM/saturated aqueous solution of NaHCO₃ (1:1, v/v) 3 times. The product was purified by column chromatography over silica gel by using n-Hexane/DCM (4:1, v/v) to give white solid product with 47.40% yield (0.39 g). This product was also synthesized with catalysts TiCl₄ and ZnCl₂ (mass of α-bromo ketone is 1g (7.336 mmol ketone with 4 equivalent zinc (1.918 g) and 2 equivalent lewis acid (1.999 ZnCl₂ and 2.783 TiCl₄) with reaction yields 51.20 % (0.423 g) and 27.30 % (0.2246 g) respectively. ¹H NMR (500 MHz, CdCl₃) δ 7.81 (d, J = 8.45 Hz, 2H), 7.79 (d, J = 8.45 Hz, 2H), 7.59 (d, J = 8.5 Hz, 2H), 7.57 (d, J = 8.3 Hz, 2H), 2.57 (s, 6H). ¹³C NMR (126 MHz, CdCl₃) δ 196.97, 196.97, 135.79, 135.79, 131.86, 131.86, 129.81, 129.81, 128.27, 128.27, 128.26, 26.52, 26.52. IR ν/ cm⁻¹: 1675.27 nm, Rf: 0.52 mp: 72.3 °C, MS (m/z): [M+1]⁺ calcd for C₁₇H₁₄BrN, 312.20; found 311.2 .

4-(3-(4-methoxyphenyl)but-2-en-2-yl)benzonitrile (5): Zinc (1.71 g, 26.19 mmol) was dissolved in dry THF (30 mL) and stirred for 30 min in an ice bath. Then, SnCl₄ (3.06 mL, 26.19 mmol) was added dropwise into the reaction mixture. The mixture was refluxed for 2 h and then cooled down to room temperature. A mixture of 4-(2-bromoacetyl)benzonitrile (0.97 g, 4.36 mmol) and 2-bromo-1-(4-methoxyphenyl)ethanone (1 g, 4.36 mmol) was dissolved in 10 mL THF and added into the reaction mixture. The reaction was stirred overnight at 75 °C. After 48 h, the reaction mixture was filtered through celite and THF was removed in a fume hood. The product was extracted with 500 mL DCM/saturated aqueous solution of NaHCO₃ (1:1, v/v) 4 times and purified by column chromatography using n-Hexane/DCM (2:1, v/v) to give pale yellow oily product with 65.25% yield (1.49 g). Product 7 was also synthesized by using ZnCl₂ as catalyst instead of SnCl₄. 1g α-bromo ketone (4.495 mmol) is used with 4 equivalent zinc (1.175 g) and 2
equivalent ZnCl₂ (1.225 g). This procedure was resulted with 65 % yield. 7 was also synthesized with TiCl₄ with 73.20 % (1.752 g) reaction yield (Equivalents are same with the reaction with ZnCl₂). ¹H NMR (500 MHz, CdCl₃) δ 8.02 (d, J = 8.45 Hz, 2H), 7.91 (d, J = 8.95 Hz, 2H), 7.75 (d, J = 8.45 Hz, 2H), 6.91 (d, J = 8.9, 2H), 3.85 (s, 3H), 2.63 (s, 3H), 2.53 (s, 3H). ¹³C NMR (126 MHz, CdCl₃) δ 196.80, 196.55, 163.46, 139.89, 132.49, 130.56, 130.29, 128.68, 117.90, 116.36, 113.66, 55.45, 26.74, 26.31. IR ν/ cm⁻¹: 1675.27 nm, Rf: 0.26, MS (m/z): [M+1]⁺ calcd for C₁₈H₁₇NO, 263.33; found, 264.2 .

4,4''-(but-2-ene-2,3-diyldianiline (6): Product 6 could not be obtained with any of the applied procedures. In these reactions, all catalysts gave 0% yield.

4',4'''-(but-2-ene-2,3-diyldibis(N,N-diphenyl-[1,1'-biphenyl]-4-amine) (7): 3 (0.3 g, 0.82 mmol) and 5 (0.76 g, 2.05 mmol) were dissolved in 30 mL of THF in a Schlenk tube under N₂ atm. Then, 5M K₂CO₃ (1.38 g K₂CO₃ in 5 mL of H₂O) was added into the Schlenk tube. The last addition is Pd(PPh₃)₄ (94 mg, 82 µmol). The tube was closed tightly and the reaction was stirred for 48 h at 75 °C. After 2 days, the reaction mixture was filtered through celite and THF was removed in a fume hood. The product was extracted with 500 mL DCM/saturated aqueous solution of NaHCO₃ (1:1, v/v) 3 times and purified by column chromatography using n-Hexane/DCM (2:1, v/v) to give yellow solid product with 36% yield (0.5 g). ¹H NMR (500 MHz, CdCl₃) δ 8.03 (d, J = 8.35 Hz, 4H), 7.67 (d, J = 8.40 Hz, 4H), 7.52 (d, J = 8.60 Hz, 4H), 7.31 (t, J = 8.2, 8H), 7.16 (d, J= 7.4 Hz, 12H), 7.07 (t, J= 7.40, 4H) 2.64 (s, 6H). ¹³C NMR (126 MHz, CdCl₃) δ 197.67, 148.18, 147.41, 145.19, 135.31, 133.11, 129.39, 128.97, 127.92, 126.48, 124.78, 123.37, 123.28, 26.63. IR ν/ cm⁻¹: 1675.27 nm, Rf: 0.43 mp: 109.7 °C, MS (m/z): [M+1]⁺ calcd for C₅₂H₄₂N₂, 694.90; found, 695.6 .
4-(3-(4'-(diphenylamino)-[1,1'-biphenyl]-4-yl)but-2-en-2-yl)benzonitrile (8): 4 (0.2 g, 0.64 mmol) and 5 (0.29 g, 0.76 mmol) were mixed in 25 mL of THF in a Schlenk tube under N₂ atm. After that, 5M K₂CO₃ (1.38 g K₂CO₃ in 5 mL of H₂O) was added to the mixture and then, Pd(PPh₃)₄ (74 mg, 64.06 µmol) was added and the tube was closed tightly. The reaction was stirred for 48 h at 75 °C and filtered through celite. The product was extracted with 500 mL DCM/saturated aqueous solution of NaHCO₃ (1:1, v/v) 4 times and purified by column chromatography using n-Hexane/DCM (2:1, v/v) to obtain the pure product as pale yellow solid with 96% yield (0.3 g). 

°H NMR (500 MHz, CdCl₃) δ 8.02 (d, J = 8.45 Hz, 2H), 7.67 (d, J = 8.50 Hz, 2H), 7.53 (d, J = 8.75 Hz, 2H), 7.29 (dd, J = 7.5, 7.45 Hz, 6H), 7.16 (m, 7H), 7.14 (t, J= 7.35 , 3H) 2.64 (s, 3H), 1.27(s, 3H) . 

¹³C NMR (126 MHz, CdCl₃) δ 197.72, 148.17, 147.40, 135.29, 133.10, 129.37, 128.96, 127.90, 126.47, 124.77, 123.35, 123.27, 67.78, 38.91, 30.58, 29.70, 28.99. Rₘ: 0.48 mp: 102.7 °C, MS (m/z): [M+1]⁺ calcd for C₃₅H₂₈N₂, 476.61; found 478.4 .

3. Computational Details

To further elucidate the optical and solvatochromic effects observed for the stilbene compounds under study, a DFT investigation was performed, with the aim to investigate the energetically more favorable isomers and the nature of dominant transitions in their absorption spectra. Additionally, to verify the experimental results, absorption spectra of E and Z isomers were computed. For this purpose, meta-hybrid M06-2X functional and 6-31G(d,p) basis set were used for ground-state optimizations using the Gaussian09 software package. Single point energy refinements were performed using B2PLYP, PBE1PBE and ωB97XD levels of theory to obtain relative energies of E and Z isomers. Solvent effects were taken into account employing a polarizable continuum (IEF-PCM) model. Absorption spectra were produced using Time-Dependent Density Functional Theory (TD-DFT). To include dynamic effects,
conformations for both $E$ and $Z$ isomers were generated via Wigner distribution as implemented in the Newton-X software package (performed at the M06-2X/6-31G(d,p) level of theory). Vertical transitions were convoluted using Gaussian functions of full-width at half length (FWHL) of 0.15 eV to ensure comparison with experimental data. Since the experimental spectra did not exhibit strong shifts among different solvents, only three solvents (Hexane, dioxane and $N,N$-dimethyl formamide) with largely differing polarities were studied computationally. To analyze the nature of dominant transitions in absorption spectra, Natural Transition Orbital (NTO) analysis with Tamm Dancoff Approximation (TDA) was performed and $\Phi_S$ indices, defining the overlap between detachment and attachment densities were obtained with Nancy_Ex code. Frontier molecular orbitals (FMO) were visualized with Avogadro software package.

4. Results and Discussion

4.1 Reaction Yield Results

<table>
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<tr>
<th>Non-Fluorescent Stilbenes</th>
<th>Fluorescent Stilbenes</th>
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<tr>
<td>D- $\pi$-D</td>
<td>A- $\pi$-A</td>
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<tr>
<td>$\text{(MeO-St-MeO)}$</td>
<td>$\text{(CN-St-CN)}$</td>
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<tr>
<td>D- $\pi$-A</td>
<td>D- $\pi$-D</td>
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<tr>
<td>$\text{(Br-St-Br)}$</td>
<td>$\text{(TPA-St-TPA)}$</td>
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<td>$\text{(CN-St-Br)}$</td>
<td>$\text{(CN-St-TPA)}$</td>
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<td>4</td>
<td>8</td>
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</table>

Figure 1 Chemical formulas of non-fluorescent and fluorescent compounds 1-5 and 7-8.
While SnCl\(_4\) and TiCl\(_4\) result in high reaction yields, ZnCl\(_2\) is the next promising candidate, owing to its ease of handling and hence, may be preferable over the very hazardous SnCl\(_4\) and TiCl\(_4\) reagents. In this study, it has been observed that within the used lewis acid catalysts, AlCl\(_3\) is the only catalyst, which does not work for the synthesis of stilbenes from \(\alpha\)-bromo ketones. Moreover, the performance of ZnCl\(_2\) which is less hazardous than the widely used SnCl\(_4\) and TiCl\(_4\) reagents was found to be in acceptable reaction yields (see Table 1).

To conclude, synthesis of the set of stilbene compounds with various catalysts has led us to understand the performances of the used catalysts in synthesis of target stilbenes from \(\alpha\)-bromo ketones. Correspondingly, we observed that the usage of ZnCl\(_2\) catalyst as alternative to hazardous SnCl\(_4\) and TiCl\(_4\) catalysts can be used in the synthesis of targeted stilbene compounds.

**Table 1.** Synthesis yields of compounds 1-5 with different catalysts.

<table>
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<th>Product</th>
<th>Catalysts</th>
<th>Yield</th>
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</table>
4.2 Solvatochromic Properties

Table 2. Optical properties of fluorescent and non-fluorescent stilbene derivatives in various solvents.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>ε</th>
<th>(\lambda_{\text{max}}^\text{abs} ) (nm)</th>
<th>(E_g^\text{opt} ) (eV)</th>
<th>(\lambda_{\text{max}}^\text{fl} ) (nm)</th>
<th>Stokes shift (cm(^{-1}))</th>
<th>(\lambda_{\text{max}}^\text{abs} ) (nm)</th>
<th>(E_g^\text{opt} ) (eV)</th>
<th>(\lambda_{\text{max}}^\text{fl} ) (nm)</th>
<th>Stokes shift (cm(^{-1}))</th>
<th>(\lambda_{\text{max}}^\text{abs} ) (nm)</th>
<th>(E_g^\text{opt} ) (eV)</th>
<th>(\lambda_{\text{max}}^\text{fl} ) (nm)</th>
<th>Stokes shift (cm(^{-1}))</th>
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<tr>
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<td>240</td>
<td>4.04</td>
<td>372, 557</td>
<td>23000</td>
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<tr>
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<td>3.93</td>
<td>366</td>
<td>6669</td>
<td>343, 372</td>
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<tr>
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<td>300, 364</td>
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</table>

<table>
<thead>
<tr>
<th>Solvent</th>
<th>ε</th>
<th>(\lambda_{\text{max}}^\text{abs} ) (nm)</th>
<th>(E_g^\text{opt} ) (eV)</th>
<th>(\lambda_{\text{max}}^\text{fl} ) (nm)</th>
<th>Stokes shift (cm(^{-1}))</th>
<th>(\lambda_{\text{max}}^\text{abs} ) (nm)</th>
<th>(E_g^\text{opt} ) (eV)</th>
<th>(\lambda_{\text{max}}^\text{fl} ) (nm)</th>
<th>Stokes shift (cm(^{-1}))</th>
<th>(\lambda_{\text{max}}^\text{abs} ) (nm)</th>
<th>(E_g^\text{opt} ) (eV)</th>
<th>(\lambda_{\text{max}}^\text{fl} ) (nm)</th>
<th>Stokes shift (cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hexane</td>
<td>2 (MeO-St-MeO)</td>
<td>1.89</td>
<td>343</td>
<td>3.17</td>
<td>238</td>
<td>4.10</td>
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<td>4.37</td>
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<tr>
<td>Toluene</td>
<td>2 (MeO-St-MeO)</td>
<td>2.38</td>
<td>342, 367</td>
<td>3.13</td>
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<td>3.76</td>
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<tr>
<td>DCM</td>
<td>2 (MeO-St-MeO)</td>
<td>8.93</td>
<td>269, 322</td>
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<tr>
<td>THF</td>
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<td>7.58</td>
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<td>253, 297</td>
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<td>Dioxane</td>
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<td>Acetone</td>
<td>2 (MeO-St-MeO)</td>
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<td>298, 337</td>
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<td>DMF</td>
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<td>36.7</td>
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<td>3.88</td>
<td>285, 337</td>
<td>3.14</td>
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</table>

*St refers to stilbene backbone. Optical band gaps \(E_g^\text{opt} \) are computed from UV-Vis absorption spectra with Tauc method.51

The solvatochromic properties of compounds 1-5, 7 and 8 were investigated in eight different solvents with differing polarities. Table 2 shows the wavelengths of maximum absorptions obtained from UV-Vis spectra. Although no large differences were observed between the \(\lambda_{\text{max}} \) values, each compound showed different trends in solvents with different polarities. On the other hand, all stilbenes showed absorptions in the range of 200 to 450 nm. Generally, all compounds
showed multiple peaks and expected bathochromic shifts are clearly observed in D-π-A type structures.

As shown in Figure 2, going from compound 1, which is an A-π-A type structure to compounds 5 and 8, which are D-π-A type structures, $\lambda_{\text{max}}$ values increased and optical band gaps decreased. This expected trend is a consequence of increased charge transfer in D-π-A systems. Effect of donor strength in these systems was also studied by incorporating a TPA unit in place of the –OMe unit. When the two D-π-A systems, compounds 5 and 8, are compared, a clear red shift is observed in the absorption spectra of 8, which is attributed to the excellent electron donating ability of the TPA unit in D-π-A or D-A systems (for more detail, see Figures S31, S32 and S33 in supporting info). Consequently, the weaker electron donating ability of the –OMe unit resulted in a blue shift, thus a higher optical band gap.

Figure 2. UV-Vis absorption spectra of compounds 1, 5 and 8 in toluene (1 x 10^{-5} M).
Effect of incorporating two TPA units is also studied with compound 7. Compounds 7 and 8 display similar behaviors in most solvents, and we have observed that stilbene 7 with two strongly electron donating TPA units, is as effective as compound 8 in terms of decreasing optical band gap, (for more details of absorption spectra of synthesized compounds, see S29 in supporting info). Figure 3 shows emission spectra and colors of the brightest stilbenes, 7 and 8.

![Fluorescence spectra of compounds 7 and 8. The insert pictures were taken at 366 nm.](image)

**Figure 3.** Fluorescence spectra of compounds 7 and 8. The insert pictures were taken at 366 nm.

To sum up, due to the various chromophore groups, stilbene compounds were found to exhibit multiple absorption bands and the differences between A-π-A, D-π-D, D-A and D-π-A systems were observed in measured absorption spectra.

Moreover, with the help of shifts in absorption spectra, we observed the stronger electron donating ability of DPA unit over –OMe unit. Surprisingly, different polarities of solvent molecules caused no changes in some absorption spectra and all stilbene compounds were shown to have very broad, similar peaks in DCM and acetone. It is worth noting that the emission spectra
are broadened with the increase in solvent polarity. Moreover, we also investigated emission characteristics of stilbene compounds. Stilbenes 1, 7 and 8 are fluorescent compounds, their fluorescence spectra details are given in Table 3.

Figure 4 Lippert–Mataga plots for the dependence of the Stokes shift on solvent polarity function

In Figure 4, Lippert–Mataga plots representing the dependence of Stokes shift, which is defined as the difference between the position of the maximum of the absorption band and that of the fluorescence, on solvent polarity function are reported. Apparently, for both compounds, increase in orientation polarizability led to decrease in Stokes shift, indicating the presence of hypsochromically shifted emission spectra in low polarity solvents. Results from Lippert–Mataga plots are consistent with the dielectric continuum theory, where the emission energy varies inversely with the dielectric constant of the solvent.52

4.3 Aggregation Caused Quenching (ACQ) Properties

Structurally, stilbene compounds with donor and acceptor moieties increase \( \pi \)-electron delocalization of the system. Moreover, TPA moiety with its strong electron donating ability is known to enhance conjugation in organic molecules. Therefore, incorporating TPA unit in stilbene compounds is an effective strategy for developing organic systems with strong conjugation. However, as reported in literature, molecules with TPA unit may exhibit AIE or ACQ behavior in
THF/water mixtures and in solid form.\textsuperscript{53} ACQ behavior of TPA moiety arises from its affinity to pack closely leading to strong $\pi \cdots \pi$ stacking interactions in $\pi$ conjugated systems (see Figure 5).\textsuperscript{53,54}

![Figure 5 Representation of $\pi \cdots \pi$ stacking interactions for TPA moiety.](image)

To observe whether compounds 7 and 8 show such characteristics, we probed the emission behavior of stilbenes in THF/H$_2$O mixtures. For this, stock solutions with varying THF/water ratios were prepared and their fluorescence measurements were performed.

![Figure 6. ACQ spectra of compounds 7 and 8.](image)
Figure 6 shows emission intensity changes in THF/H$_2$O mixtures and it is obvious that increasing water concentration results in quenching of the emission, as expected from the TPA unit. The emissions of both compounds were dramatically weakened when water fraction reached 85%. Meanwhile, for compound 7, with the increase of water percentage from 0% to 50%, a red shift was observed from 470 nm to 548 nm. When the water fraction further increased from 50% to 95%, the fluorescence emission was blue shifted from 548 nm to 500 nm. Moreover, new absorption peaks emerge with the addition of small amounts of water, which implies that the molecules have aggregated.

For compound 8, red shifted emission from 475 nm to 564 nm was observed, until the water fraction reaches 60%, subsequently, as water ratio further increased from 60% to 85%, the spectra was blue shifted from 564 nm to 489 nm. While red shifted emission spectra is a consequence of enhanced intermolecular charge transfer effects between solutes and polar solvents, blue shifted spectra may originate from the suppression of further charge transfer.$^{55,56}$

4.4 Computational Results

It is well known that the geometry of molecule has an important influence on excited state properties, such as absorption and emission spectra of stilbene molecules. Therefore, geometry optimizations for all the synthesized stilbene molecules in the $S_0$ states were accomplished using the M062X/6-31G(d,p) level of theory. The choice of M062X functional for geometry optimizations is justified by its good performance in reproducing long-range interactions, electronic energies, and equilibrium geometries of aromatic ring systems.

Stilbene molecules are expected to have two structural isomers, $E$ and $Z$. We firstly optimized both possible isomers for the entire molecule set and by comparing their relative Gibbs Free energies, energetically more favorable geometries were determined. Figure 7A represents relative energies of the isomers computed at B2PLYP/6-31G(d,p), PBE0/6-31G(d,p), and M06-2X/6-31G(d,p) levels of theory. Apparently, except for compounds 5 and 7, $E$ isomers of synthesized stilbenes are energetically more stable compared to $Z$ isomers. However, while $E$ and $Z$ isomers of compound 5 are found to be isoenergetic, $Z$ isomer of compound 7 has
lower energy than its $E$ isomer. Therefore, it has been concluded that only these two compounds prefer $Z$ geometry. In Figure 7B, energetically more stable isomers were visualized with CYLview software package. It is quite clear that the different geometries and substituents on stilbene compounds leads to different photophysical properties.

Table 3 represents the spectral properties of highest intensity transitions such as oscillator strengths, absorption wavelengths, Phi-S indices, nature of transitions and the orbitals responsible for the transitions with highest oscillator strengths. The results presented in Table 4 show that the highest $f$ values correspond to $S_0\rightarrow S_1$ transitions with two exceptions, which are $S_0\rightarrow S_3$ transition for compound 2 and $S_0\rightarrow S_2$ transition for compound 7. Moreover, the absorption spectra are all quite similar, with absorption maxima in the range of 230–315 nm.

**Figure 7** A) Single point energies on M06-2X optimized structures in $n$-hexane solvent. 6-31G(d,p) basis set is used in all calculations. B) 3D visuals of optimized isomers generated with CYLview software package.

**Table 3** Theoretical photophysical properties computed at M062X/6-31G(d,p) level of theory in $n$-hexane solvent.
Though theoretical absorption spectra could not reproduce experimental spectra perfectly, absolute deviations are in the range of 10–40 nm which is a situation which does not affect the usage areas. (see Figure S29). Additionally, going from A-\pi-A to A-\pi-D systems, stronger conjugation effects have been observed as bathochromic shifts in absorption spectra.

As reported in Table 3, when compared to compound 5-E (A-\pi-D), compound 1-E (A-\pi-A) has a hypsochromically shifted absorption spectrum and the same trend is observed in compounds 7 and 8 which have \( \lambda_{\text{max}} \) values as 307.13 nm and 314.99 nm respectively. Therefore, in contrast to the 10–40 nm spectral shifts, theoretical \( \lambda_{\text{max}} \) values support the expected wavelength shifts between A-\pi-A and A-\pi-D systems.

![Diagram of molecules and orbital transitions](image)

**Figure 8** Natural transition orbitals computed at M062X/6-31G(d,p) level of theory.
To investigate the natures of vertical transitions with highest $f$ values, $\Phi_S$ indices were reported and the reorganization of electronic density has been analyzed (see Table 4 and Figure 8). $\Phi_S$ index can be used to measure the degree of overlap between the frontier molecular orbitals responsible for relevant transitions.

Importantly, all $\Phi_S$ indices are in the range of 0.7607–0.9134, indicating dominant local excitation (LE) characters of transitions from stilbene compounds. Accordingly, since transitions in LE character are observed as high intensity bands in absorption spectrum, our theoretical findings from $\Phi_S$ indices and the reorganization of electronic density are consistent with the high intensity absorptions in experimental spectra (see Figure S29). Moreover, $f$ values between 0.2000 and 1.0000 implies that there are no charge transfer transitions in these stilbene compounds. This observation is consistent with small torsion angles within the molecules, which lead to large overlap between the frontier molecular orbitals (see Table S1).

5. Conclusion

Five different stilbene compounds were synthesized via the McMurry coupling reaction, using different catalysts, and their solvatochromic properties were examined in solvents with varying polarities. Two stilbene compounds with TPA unit were synthesized via Suzuki Coupling. The most effective synthesis procedure is suggested to be with SnCl$_4$ and ZnCl$_2$. While SnCl$_4$ works well in the synthesis of all stilbenes, ZnCl$_2$ is the new promising candidate, owing to its ease of handling. Results reveal that TPA containing stilbenes (7 and 8) exhibit excellent fluorescence properties, a trend which can be attributed to the strong electron donating ability of the TPA unit and the effective charge transfer within these molecules. Although the compounds without TPA unit have no emission properties, they exhibit different behaviors in solvents with different polarities. Aggregation caused quenching properties of TPA consisting molecules (7 and 8) were
also studied and increasing water concentrations led to decreased emissions in both compounds. Moreover, a computational study was performed to investigate the absorption spectra features theoretically. FMO distributions and \( \Phi_s \) indices for dominant transitions with large oscillator strength indicate that the stilbene compounds under investigation exhibit transitions in LE character. To sum up, a new synthesis procedure for stilbenes was developed and it is shown that suitable modifications may lead to light emitting stilbene compounds for various applications. Moreover, the \( Z \)-isomer of stilbene 5 is an especially suitable candidate for cancer treatments due to higher anti-metastatic activity compared its \( E \)-isomer [11].

To conclude, herein, we represent a comprehensive experimental and computational photophysical property analyses for the set of stilbenes under investigation. Synthesis part of this study shed light to the comparisons between various reaction procedures and proposed the environmentally friendly, less hazardous catalyst \( \text{ZnCl}_2 \) for the researchers studying in this area. Moreover, solvatochromism and ACQ measurements supported by the Lippert-Mataga plots represents the polarity dependency of absorption-emission spectra of these kinds of organic molecules and the behavior of TPA moiety in stilbene compounds respectively. On the other hand, computational protocols used in this study are highly important to understand the photophysical processes observed in an absorption spectrum. To sum up, there were two main goals in this study; 1) finding and environmentally friendly, easy to handle catalyst for the synthesis procedures, 2) understanding the photophysical properties of stilbene compounds. At the end of this study, we presented comprehensive results and shed light on the future studies that will be performed on this topic.
SUPPORTING INFORMATION

NMR, IR and GC-MASS Spectra of all compounds, spectroscopic data, level of theory study, calculated absorption spectra and Cartesian coordinates of optimized structures.

ACKNOWLEDGEMENT

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Erdal Ertas: 0000-0002-9736-0824

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