Structural and physical properties of triarylamines bearing alkyl chains introduced by strontium-mediated alkylation

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Abstract

Introducing alkyl chains into π-conjugated organic molecules is a well-established strategy for tuning solubility, crystallinity, and photophysical properties without significantly perturbing their electronic structures. However, conventional alkylation methods, such as the Grignard reaction, often fail to achieve efficient functionalization when applied to sterically hindered aromatic systems, such as triarylamines, which are widely used as building blocks in electronic materials. In this study, a strontium-mediated alkylation reaction was employed to introduce linear and branched alkyl chains at the para-positions of triarylamine derivatives bearing methoxycarbonyl groups. This method enables efficient alkylation under mild conditions, even at sterically congested benzylic positions. A series of alkylated triarylamines was synthesized using various alkyl iodides and metallic strontium. The resulting compounds were fully characterized by NMR, IR, and high-resolution mass spectrometry. Their electronic and luminescent properties were investigated by UV-Vis absorption and fluorescence spectroscopy in various solvents. Although the absorption maxima shifted only slightly depending on the alkyl substituent, indicating minimal perturbation of the π-conjugated backbone, fluorescence measurements revealed a pronounced dependence of the quantum yield on the length and branching of the alkyl chains. In particular, the introduction of bulky substituents such as neopentyl groups led to a significant decrease in emission efficiency, likely due to steric hindrance and enhanced nonradiative decay pathways. These findings demonstrate that long-chain and branched alkyl substituents serve as subtle yet effective modulators in modulating the photophysical behavior of triarylamines. Overall, strontium-mediated alkylation offers a robust functionalization strategy for modifying the periphery of triarylamine frameworks while preserving their core conjugation. This approach, which enables the introduction of bulky alkyl groups inaccessible via conventional methods, opens new avenues for designing functional organic materials with tunable electronic properties.

Key words
alkylation, metallic strontium, luminescence properties, triarylamine, substituent effect

1. Introduction

Triarylamines are one of the most widely studied organic molecules and have potential applications in photoelectric properties. They have been used extensively to manufacture various types of electronic devices, mainly or partially based on organic electroactive components (Agarwala et al., 2017; Grigoras et al., 2014; Hüttner et al., 2010; Kroeze et al., 2006; Santra et al., 2016; Shirota 2000). Varying the structure of the linked functional units allows the tuning of the electronic or physical properties of the triarylamine (Bhagwat et al., 2019; Guo et al., 2014; Neubauger et al., 2009; Retiig, 1986; van Walree et al., 2004; Zúñiga-Núñez et al., 2018). In a previous paper, we reported the structural and electronic properties of triarylamines, whose conformations are twisted due to the steric effect introduced by the methoxycarbonyl groups (Ohmura et al., 2019). On the other hand, π-conjugated compounds often exhibit poor solubility or high crystallinity based on their rigid and highly planar structure. To improve their unfavorable performance, introducing alkyl chains is widely used (Chai et al., 2015; Lei et al., 2014; Osaka et al., 2014).

On the other hand, organometallic compounds are some of the most versatile reagents for organic synthesis. For example, numerous reports have been published on the Grignard reaction, which utilizes metallic magnesium and alkyl halides. These include well-established methods for the alkylation of carbonyl compounds using Grignard reagents, which proceed smoothly to afford the corresponding adducts in good yields (Wakefield, 1995). Moreover, as a Grignard reagent is commercially available, the Grignard reagent is a candidate method for introducing an alkyl chain at a position adjacent to the benzene ring. However, the reactions of the Grignard reagents are diminished when using bulky substrates or bulky Grignard reagents. Indeed, previous reports have found that the Grignard method is less reactive when using bulky substrates and bulky Grignard reagents (Miyoshi et al., 2005b; Ohmura et al., 2017).

Meanwhile, reactions using an organometallic compound composed of an alkaline earth element other than magnesium have been reported (Lindsell, 1982; 1995; Miyoshi 2004; Yanagisawa and Yoshida, 2011; Yanagisawa et al., 2016). Among them, we are focusing on the reactions using metal strontium and developing research. A few reports have been found in the studies on the reactivity of organostrontium species in organic synthesis (Agostinho and Kobayashi, 2008; Barrett et al., 2008; Datta et al., 2008; Gowenlock et al., 1975; Liu et al., 2012; Sell and Rieke, 1995), except for our study (Miyoshi et al., 2004; 2005a; 2005b; 2012; 2020; Ohmura et al., 2017; 2018). We have been investigating synthetic reactions using metallic strontium as a reagent and have reported that the alkylation of aldehydes, imines, ketones, or esters with alkyl iodides, as well as the dialkylation of esters with alkyl iodides, proceeds smoothly using metallic strontium to afford the corresponding adducts in good yields. Using the strontium method, the reaction, as a one-pot protocol, proceeds smoothly at a mild temperature to give the corresponding adduct in excellent yield via the so-called Barbier procedure. For the demonstration of the utility of the strontium method, we have focused on 4,4′,4″-nitrilotris(benzenemethanol) skeleton and embarked upon introducing alkyl groups. Although there are a few reports of arylated compounds (Hellwinkel et al., 1983; Strohbusch and Zimmermann, 1969), no reports exist of introducing an alkyl group at the benzylic positions. Herein, we synthesized triarylamine derivatives bearing alkyl groups introduced by the strontium method and investigated their structural and electronic properties.

2. Experimental procedure

2.1 General methods

All reagents and solvents were purchased from commercial sources and were further purified by standard methods, if necessary. ^{1}H (400 MHz) and ^{13}C (100 MHz) NMR spectra were recorded with a JEOL JNM-ECS 400 spectrometer and chemical shifts were reported in ppm using tetramethylsilane as an internal standard. Infrared spectra were recorded on SHIMADZU FTIR 8400 spectrometer. HRMS spectra obtained Waters Xevo Q-TOF MS. UV-Vis spectra were recorded with a Hitachi U-3500 spectrometer in deaerated pure solvents under argon at 298 K. Emission spectra were recorded with a SHIMADZU RF-5300PC spectrofluorophotometer in deaerated pure solvents under argon at 298 K. UV-Vis and emission spectra measurements were conducted using 1 cm path-length quartz cuvettes.

2.2 Sample preparation

2.2.1 Synthesis of triarylamine derivative 1

The synthetic method was previous literature (Walker et al., 2009) and characterized by ^{1}H and ^{13}C NMR, FT-IR and HRMS spectroscopically.

- Triarylamine derivative 1:
  yield: 84 %; ^{1}H-NMR (400 MHz, $CDCl_3$): $\delta = 7.96$ (d, 6H, $J = 8.4$ Hz), 7.13 (d, 6H, $J = 8.8$ Hz), 3.91 (s, 9H); ^{13}C-NMR (100 MHz, $CDCl_3$): 166.4, 150.3, 131.2, 125.4, 123.8, 52.0 ppm; IR (KBr): $\nu = 3001$, 2951, 2844, 2562, 1931, 1731, 1594, 1505, 1430, 1317, 1271, 1171, 1107, 1012 cm^{-1}; HRMS (EI): *m/z*: calcd for $C_{24}H_{22}NO_6$: 420.1461 $[M+H]^+$; found 420.1451.

2.2.2 Synthesis of triarylamine derivatives 2-5

Under an argon atmosphere, metallic strontium (9.0 mmol) was added to an anhydrous THF (5 mL) suspension of triarylamine derivative 1 (1.0 mmol) and corresponding alkyl iodide (9.0 mmol) at ambient temperature. After stirring, the reaction mixture was quenched by 1 M HCl aqueous solution (15 mL). The organic materials were extracted with diethyl ether (15 mL) three times, and the combined organic layers were washed successively with 5 % of $KHSO_3$ solution, brine, respectively and dried over anhydrous Na_2SO_4. After evaporation of the solvent, the residue was purified by column chromatography on silica gel (hexane/ethyl acetate) to give the corresponding compounds shown in Figure 1. All compounds were fully characterized by ^{1}H and ^{13}C NMR, FT-IR and HRMS spectroscopically.

- Triarylamine derivative 2:
  yield: 36 %; ^{1}H-NMR (400 MHz, $CDCl_3$): $\delta = 7.23$ (d, 6H, $J = 8.4$ Hz), 7.03 (d, 6H, $J = 8.8$ Hz), 1.78 (t, 12H, $J = 6.0$, 4.8 Hz), 1.67 (brs, 3H), 1.28-1.13 (m, 26H), 0.87 (t, 18H, $J = 7.2$ Hz); ^{13}C-NMR (100 MHz, $CDCl_3$): 145.9, 140.7, 126.0, 123.3, 76.8, 42.4, 25.7, 23.1, 14.1 ppm; IR (KBr): $\nu = 3500$, 3031, 2934, 2860, 1602, 1505, 1489, 1455, 1378, 1319, 1271, 1179, 1151, 1110, 1015 cm^{-1}; HRMS (EI): *m/z*: calcd for $C_{45}H_{70}NO_3$: 672.5356 $[M+H]^+$; found 672.5379.

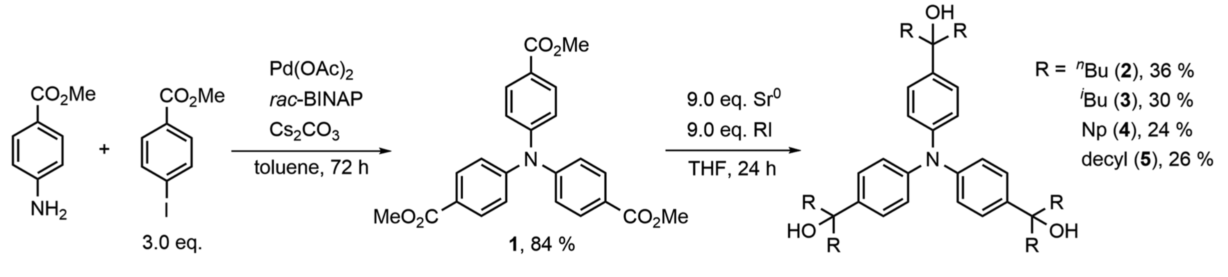

Figure 1: Synthesis of triarylamine derivatives 2-5 bearing alkyl chains via triarylamine derivative 1

- Triarylamine derivative 3:
  yield: 30 %; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.24 (d, 6H, J = 8.8 Hz), 7.01 (d, 6H, J = 8.4 Hz), 1.78-1.61 (m, 21H), 0.92 (d, 18H, J = 6.4 Hz), 0.71 (d, 18H, J = 6.4 Hz); ^{13}C-NMR (100 MHz, $CDCl_3$): 145.8, 140.6, 126.2, 123.2, 77.9, 52.7, 24.6, 24.5, 23.9 ppm; IR (KBr): ν = 3610, 3035, 2950, 2901, 2866, 1717, 1602, 1575, 1505, 1366, 1320, 1278, 1156, 1111, 1057 cm^{-1}; HRMS (EI): *m/z*: calcd for $C_{45}H_{70}NO_3$: 672.5356 [M+H]$^+$; found 672.5326.
- Triarylamine derivative 4:
  yield: 24 %; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.31 (brs, 6H), 6.96 (d, 6H, J = 7.6 Hz), 1.90 (d, 6H, J = 14.8 Hz), 1.74 (d, 6H, J = 16.0 Hz), 0.78 (s, 54H); ^{13}C-NMR (100 MHz, $CDCl_3$): 145.7, 140.1, 126.9, 122.8, 79.0, 57.8, 31.9, 31.6 ppm; IR (KBr): ν = 3710, 2950, 2867, 1605, 1507, 1363, 1319, 1276, 1244, 1182, 1094, 1016, 937 cm^{-1}; HRMS (EI): *m/z*: calcd for $C_{51}H_{82}NO_3$: 756.6295 [M+H]$^+$; found 756.6297.
- Triarylamine derivative 5:
  yield: 26 %; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.25 (d, 6H, J = 8.4 Hz), 7.04 (d, 6H, J = 8.4 Hz), 1.81-1.79 (m, 12H), 1.70 (brs, 3H), 1.27-1.16 (m, 96H), 0.90 (t, 18H, J = 6.8, 6.0 Hz); ^{13}C-NMR (100 MHz, $CDCl_3$): 145.9, 140.7, 126.0, 123.3, 76.8, 42.6, 31.9, 30.0, 29.6, 29.5, 29.3, 23.5, 22.7, 14.1 ppm; IR (KBr): ν = 3425, 2923, 2852, 1602, 1505, 1455, 1318, 1275, 1183, 1016, 890 cm^{-1}; HRMS (EI): *m/z*: calcd for $C_{81}H_{141}NO_3$: 1176.0911 [M]$^+$; found 1176.0912.

3. Result and discussion

Triarylamine derivative 1, bearing methoxycarbonyl groups at the para positions of the benzene rings, was synthesized via a palladium-catalyzed coupling reaction between methyl 4-iodobenzoate and methyl 4-aminobenzoate, as previously reported (Walker et al., 2009). Alkylation of this compound using the strontium-mediated Barbier-type reaction with various alkyl iodides provided triarylamine derivatives 2–5 (Figure 1). The resulting products were fully characterized by ^{1}H and ^{13}C NMR, IR, and HRMS spectroscopy. Triarylamine derivatives with linear alkyl chains (2 and 5) were obtained as highly viscous oils, while those with branched chains (3 and 4) were isolated as white solids. This difference in physical state is likely due to the molecular packing and steric bulk of the alkyl groups.

The electronic absorption properties of the compounds were investigated by UV-Vis spectroscopy in dichloromethane (Figure 2 (a)). In this measurement, a 1.0 x 10^{-5} M solution in dichloromethane was used under an argon atmosphere at 298 K with 1 cm pathlength quartz cuvettes. The spectra of triarylamines 1-5 are shown in Figure 2 (a). All triarylamines (1–5) exhibited absorption bands in the range of 300–350 nm, which are attributed to $\pi \rightarrow \pi^*$ transitions between the benzene rings and the central nitrogen atom (Chen et al., 2010). Notably, triarylamines 2–5 exhibited a slight blue shift in the absorption maxima compared to triarylamine 1. This shift may result from the loss of the electron-withdrawing methoxycarbonyl group, which originally promoted a push-pull electronic effect in triarylamine 1. Interestingly, a subtle red shift in the absorption maxima was observed with increasing alkyl chain length among triarylamines 2, 3 and 5. Similar bathochromic behavior has been reported for pyrene and fluorescein derivatives with alkyl substitution, where extended alkyl chains induce slight perturbations in π-conjugation (Niko et al., 2013). This suggests that the alkyl groups in triarylamines may also influence the conjugated backbone through conformational or electronic effects, albeit to a modest extent.

The luminescence properties were further evaluated in different solvents (cyclohexane, dichloromethane and acetonitrile), as shown in Figures 2 (b)-(f) and summarized in Table 1. Figures 2 (b)-(f) present the normalized emission spectra of triarylamines 1-5, respectively. Measurements were performed in deaerated solvents under argon at 298 K, using excitation wavelength of 351 nm for triarylamine 1, 308 nm for triarylamine 2, 310 nm for triarylamine 3, 312 nm for triarylamine 4 and 319 nm for triarylamine 5. In all cases, the emission spectra exhibited slight red shifts with increasing solvent polarity, indicating weak but observable solvatochromic behavior. This effect was particularly prominent in triarylamine 1, which showed both the highest quantum yield and the largest solvatochromic shift among the triarylamines. By contrast, triarylamine 4 exhibited minimal spectral shifts across solvents, which may reflect its restricted conformational flexibility due to the bulky neopentyl groups. Triarylamine 1 exhibited the highest quantum yield (Φ_F = 0.59 in cyclohexane), along with clear solvatochromic behavior. The introduction of alkyl chains (triarylamines 2-5) generally led to decreased quantum yields, likely due to the increased flexibility of the alkyl substituents, which enhances non-radiative decay pathways (Kitamura, 2012; Tang and Qin, 2013). Among the alkylated derivatives, triarylamine 4, bearing a neopentyl group, exhibited the lowest fluorescence quantum yields across all tested solvents. This phenomenon is likely due to the significant steric hindrance introduced by the bulky neopentyl group, which may restrict the effective conjugation between the central nitrogen atom and the aromatic rings. Such steric constraints can induce conformational twisting, thereby reducing planarity and impairing π-conjugation—an effect known to diminish radiative transitions and enhance non-radiative decay. This interpretation is supported by previous studies on sterically hindered aromatic systems, where bulky alkyl substituents were shown to disturb coplanarity and suppress fluorescence emission (Kitamura, 2012; Tang and Qin, 2013). For instance, Kitamura reported that tetracene derivatives with bulky alkyl chains exhibited decreased fluorescence yields due to disrupted intermolecular packing

Table 1: Solvatochromic emission data for triarylamines 1-5

Triarylamine	Φ_F*, λ_{max}		
	cyclohexane	dichloromethane	acetonitrile
1	0.59, 366 nm	0.39, 409 nm	0.30, 423 nm
2	0.20, 377 nm	0.17, 405 nm	0.21, 399 nm
3	0.17, 372 nm	0.22, 392 nm	0.15, 375 nm
4	0.07, 366 nm	0.03, 383 nm	0.08, 374 nm
5	0.19, 375 nm	0.16, 403 nm	0.18, 386 nm

Note: The relative fluorescence quantum yield was determined with quinine sulfate (λ_{ex} = 350 nm).

and internal torsion. Similar steric effects have also been discussed in aggregation-induced emission (AIE) systems, where conformational restriction plays a critical role in modulating luminescence behavior (Tang and Qin, 2013). Thus, the low fluorescence efficiency of triarylamine 4 is consistent with known steric inhibition effects and highlights the sensitivity of triarylamine emission to conformational freedom and substitution pattern. These findings suggest that both the length and branching of the alkyl chain influence the photophysical behavior of triarylamines, although the impact remains moderate.

Overall, the spectroscopic results suggest that alkylation via the strontium method enables structural modification of triarylamines without drastically altering their electronic properties. However, the alkyl groups can fine-tune solubility, physical state, and luminescence efficiency, which is valuable for designing functional materials.

4. Conclusion

In this study, we successfully synthesized a series of novel triarylamine derivatives bearing linear and branched alkyl chains through a strontium-mediated Barbier-type alkylation method. The reactions proceeded under mild conditions and provided the desired products with moderate yields, demonstrating the versatility of metallic strontium for introducing alkyl groups even at sterically hindered benzylic positions. Spectroscopic characterization revealed that the core electronic structures of the triarylamine skeletons were largely preserved after alkylation, as evidenced by only minor shifts in the UV-Vis absorption spectrum. However, fluorescence measurements indicated that the introduction of flexible or bulky alkyl chains affected the emission efficiency, particularly in the case of the neopentyl-substituted derivative, which showed a pronounced decrease in quantum yield due to steric hindrance. These findings highlight that while strontium-mediated alkylation enables structural tuning without drastic disruption of the conjugated system, subtle photophysical properties can still be modulated by selecting alkyl substituents. Moreover, the methoxycarbonyl group proved to be an effective anchor for site-selective alkylation using the strontium method.

We anticipate that this strategy will apply to other π-conjugated molecular systems, including more rigid or

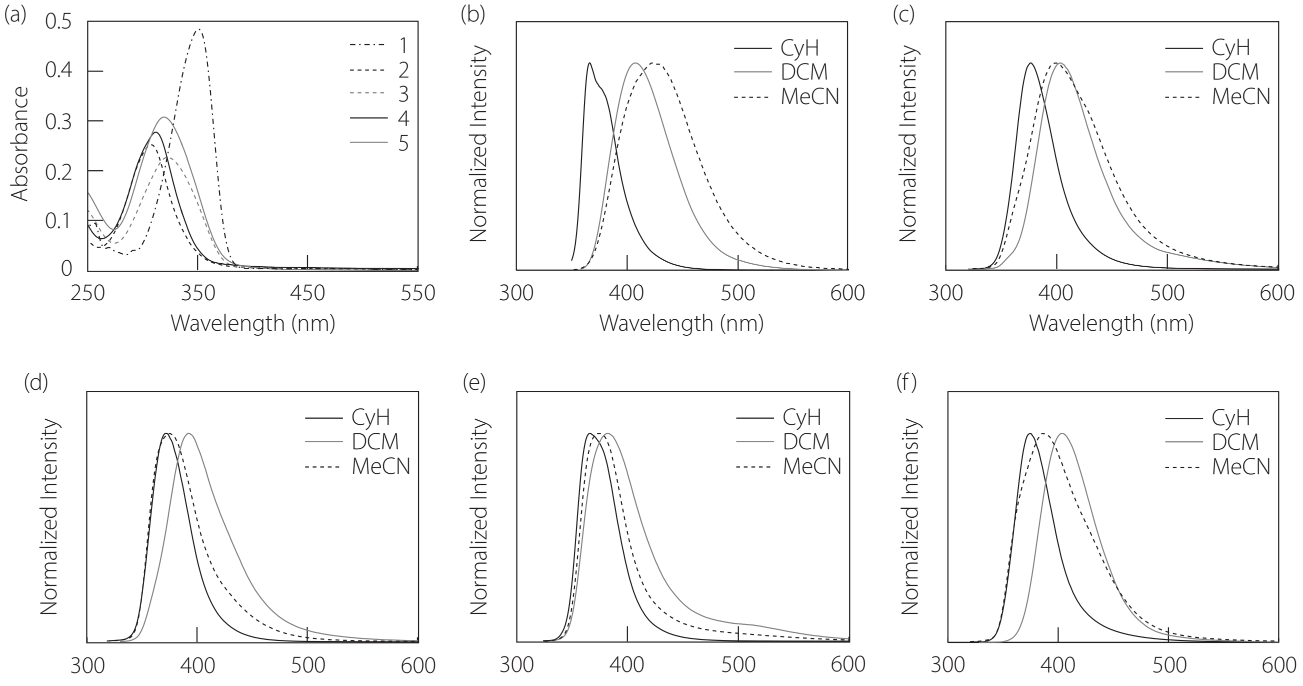

Figure 2: (a) The electronic spectra of triarylamine derivatives 1-5 in CH_2Cl_2 (1.0×10^{-5} M). The normalized emission spectra of (b) 1 (λ_{ex} = 351 nm), (c) 2 (λ_{ex} = 308 nm), (d) 3 (λ_{ex} = 310 nm), (e) 4 (λ_{ex} = 312 nm), (f) 5 (λ_{ex} = 319 nm) in cyclohexane (CyH), dichloromethane (DCM) and acetonitrile (MeCN) at ambient temperature

functionally dense frameworks. Further investigations are ongoing to explore how such alkylation can influence the optoelectronic behavior of more complex conjugated architectures via post-functionalization through the methoxycarbonyl moiety.

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References

Agarwala, P. and Kabra, D. (2017). A review on triphenylamine (TPA) based organic hole transport materials (HTMs) for dye sensitized solar cells (DSSCs) and perovskite solar cells (PSCs): Evolution and molecular engineering. *Journal of Materials Chemistry A*, Vol. 5, pp. 1348-1373.

Agostinho, M. and Kobayashi, S. (2008). Strontium-catalyzed highly enantioselective Michael additions of malonates to enones. *Journal of the American Chemical Society*, Vol. 130, pp. 2430-2431.

Barrett, A. G. M., Crimmin, M. R., Hill, M. S., Hitchcock, P. B., Kociok-köhn, G., and Procopiou, P. A. (2008). Triazenide complexes of the heavier alkaline earths: synthesis, characterization, and suitability for hydroamination catalysis. *Inorganic Chemistry*, Vol. 47. pp. 7366-7376.

Bhagwat, A. A. and Sekar, N. (2019). Fluorescent 7-substituted coumarin dyes: solvatochromism and NLO studies. *Journal of Fluorescence*, Vol. 29, pp. 121-135.

Chai, Z., Wu, M., Fang, M., Wan, S., Xu, T., Tang, R., Xie, Y., Mei, A., Han, H., Li, Q., and Li, Z. (2015). Similar or totally different: The adjustment of the twist conformation through minor structural modification, and dramatically improved performance for dye-sensitized solar cell. *Advanced Energy Materials*, Vol. 5, 1500846.

Chen, W. H., Wang, K. L., Hung, W. Y., Jiang, J. C., Liaw, D. J., Lee, K. R., Lai, J. Y., and Chen, C. L. (2010). Novel triarylamine-based alternating conjugated polymer with high hole mobility: Synthesis, electro-optical, and electronic properties. *Journal of Polymer Science, Part A: Polymer Chemistry*, Vol. 48, pp. 4654-4667.

Datta, S., Gamer, M. T., and Roesky, P. W. (2008). Aminotroponiminate complexes of the heavy alkaline earth and the divalent lanthanide metals as catalysts for the hydroamination/cyclization reaction. *Organometallics*, Vol. 27, pp. 1207-1213.

Gowenlock, G., Lindsell, W. E., and Singh, B. (1975). Preparation an disolation of alkyliodostrontium and alkyliodobarium compounds. *Journal of Organometallic Chemistry*, Vol. 101, pp. C37-C39.

Grigoras, M., Ivan, T., Vacareanu, L., Catargiu, A. M., and Tigoianu, R. (2014). Synthesis and optoelectronic characterization of some triphenylamine-based compounds containing strong acceptor substituents. *Journal of Luminescence*, Vol. 153, pp. 5-11.

Guo, Z. H., Jin, Z. X., Wang, J. Y., and Pei, J. (2014). A donor–acceptor–donor conjugated molecule: Twist intramolecular charge transfer and piezochromic luminescent properties. *Chemical Communications*, Vol. 2014, pp. 6088-6090.

Hellwinkel, D., Stahl, H., Gaa, H. G., and Gottfried, R. (1983). Novel colored systems of the "inverted triphenylmethylium dye" type containing nitrogen, phosphorus, sulfur and congeneric donor centers. *Phosphorus and Sulfur and the Related Elements*, Vol. 18, pp. 121-124.

Hellwinkel, D., Stahl, H., and Gaa, H. G. (1987). Tieffarbige, durchkonjugierte multi-triphenylmethylium-ionen. *Angewante Chemie*, Vol. 99, pp. 822-823.

Hüttner, S., Sommer, M., Steiner, U., and Thelakkat, M. (2010). Organic field effect transistors from triarylamine side-chain polymers. *Applied Physical Letters*, Vol. 96, No. 073503.

Kitamura, C. (2012). Tuning the solid-state optical properties of tetracene derivatives by modification of the alkyl side-chains: crystallochromy and the highest fluorescence quantum yield in acenes larger than anthracene. *The Chemical Record*, Vol. 12, pp. 506-514.

Kroeze, J. E., Hirata, N., Schmidt-Mende, L., Orizu, C., Ogier, S. D., Karr, K., Grätzel, M., and Durrant, J. R. (2006). Parameters influencing charge separation in solid-state dye-sensitized solar cells using novel hole conductors. *Advanced Functional Materials*, Vol. 16, pp. 1832-1838.

Lei, T., Wang, J. Y., and Pei, J. (2014). Roles of flexible chains in organic semiconducting materials. *Chemistry of Materials*, Vol. 26, pp. 594-603.

Lindsell, W. E. (1982). Chapter 4 - Magnesium, calcium, strontium and barium. In *Comprehensive organometallic chemistry: The synthesis, reactions and structure of organometallic compounds*, Vol. 1, pp. 155-252. Pergamon Press.

Lindsell, W. E. (1995). Chapter 3 - Magnesium, calcium, strontium and barium. In *Comprehensive organometallic chemistry II*, Vol. 1, pp. 57-127. Pergamon Press.

Liu, B., Roisnel, T., Carpentier, J. F., and Sarazin, Y. (2012). When bigger is better: intermolecular hydrofunctionalizations of activated alkenes catalyzed by heteroleptic alkaline earth complexes. *Angewante Chemie International Edition*, Vol. 51, pp. 4943-4946.

Miyoshi, N. (2004). Category 1: Organometallics; 7.8 product class 8: strontium compounds. In *Science of synthesis*, Vol. 7, pp. 685-694. Thieme Press.

Miyoshi, N., Kamiura, K., Oka, H., Kita, A., Kuwata, R., Ikehara, D., and Wada, M. (2004). The Barbier-type alkylation of aldehydes with alkyl halides in the presence of metallic strontium. *Bulletin of the Chemical Society of Japan*, Vol. 77, pp. 341-345.

Miyoshi, N., Ikehara, D., Kohno, T., Matsui, A., and Wada M.

(2005a). The chemistry of alkylstrontium halide analogues: Barbier-type alkylation of imines with alkyl halides. *Chemistry Letters*, Vol. 34, pp.760-761.

Miyoshi, N., Matsuo, T., and Wada, M. (2005b). The chemistry of alkylstrontium halide analogues, Part 2: Barbier-type dialkylation of esters with alkyl halides. *European Journal of Organic Chemistry*, Vol. 2005, pp. 4253-4255.

Miyoshi, N., Matsuo, T., Mori, M., Matsui, A., Kikuchi, M., and Wada, M. (2009). A new synthetic method for para alkylation of benzoic acids using metallic strontium and alkyl iodide. *Chemistry Letters*, Vol. 38, pp. 996-997.

Miyoshi, N., Asaoka, M., Miyazaki, Y., Tajima, T., Kikuchi, M., and Wada, M. (2012). The convenient and useful esterification of bulky tertiary alcohols using strontium compounds. *Chemistry Letters*, Vol. 41, pp. 35-36.

Miyoshi, N., Kimura, S., Kubo, S., Ohmura, S. D., and Ueno, M. (2020). Chemoselective ketone synthesis by the strontium-mediated alkylation or arylation of N,N-dimethylamides or urea. *Asian Journal of Organic Chemistry*, Vol. 9, pp. 1660-1664.

Neubauger, A., Bendig, J., and Rettig, W. (2009). Control of charge transfer by conformational and electronic effects: Donor–donor and donor–acceptor phenyl pyrroles. *Chemical Physics*, Vol. 358, pp. 235-244.

Niko, Y. Kawauchi, S., Otsu, S., Tokumaru, K., and Konishi, G. (2013). Fluorescence enhancement of pyrene chromophores induced by alkyl groups through σ–π conjugation: systematic synthesis of primary, secondary, and tertiary alkylated pyrenes at the 1, 3, 6, and 8 positions and their photophysical properties. *The Journal of Organic Chemistry*, Vol. 78, pp. 3196-3207.

Ohmura, S. D., Miyazaki, Y., Kanehiro, D., Yamaguchi, Y., Kitakata, S., Tateda, S., Nishizawa, T., Shimoda, R., Nagaoka, G., Ueno, M., and Miyoshi, N. (2017). Superior alkylating agents for bulky esters/ketones via strontium-mediated Barbier-type reaction. *Asian Journal of Organic Chemistry*, Vol. 6, pp. 821-824.

Ohmura, S. D., Ueno, M., and Miyoshi, N. (2018). Strontium-mediated selective protonation of unsaturated linkage of aromatic hydrocarbons and these derivatives. *Tetrahedron Letters*, Vol. 59, pp. 2268-2271.

Ohmura, S. D., Yamana, K., Ueno, M., and Miyoshi, N. (2019). Methoxycarbonyl group as a conformational regulator for the benzene ring of triphenylamines. *ChemisrySelect*, Vol. 4, pp. 3799-3802.

Osaka, I., Saito, M., Koganezawa, T., and Takimiya, K. (2014). Thiophene-thiazolothiazole copolymers: significant impact of side chain composition on backbone orientation and solar cell performances. *Advanced Materials*, Vol. 26, pp. 331-338.

Santra, D. C., Mondal, S., and Malik, S. (2016). Design of triphenylamine appended anthracene derivatives: electro-polymerization and their electro-chromic behavior. *RSC Advances*, Vol. 2016, pp.81597-81606.

Sell, M. S. and Rieke, R. D. (1995). Carbocyclization of E,E-1,4-diphenyl-1,3-butadiene with dichloroalkanes mediated by Rieke metals. *Synthetic Communications*, Vol. 25, pp. 4107-4113.

Shirota, Y. (2000). Organic materials for electronic and optoelectronic devices. *Journal of Material Chemistry*, Vol. 10, pp. 1-25.

Strohbusch, F. and Zimmermann, H. (1969). Über heteroverknüpfte triphenylmethylradikale und-carboniumionen. *Tetrahedron Letters*, Vol. 10, pp. 1705-1708.

Tang, B. Z. and Qin, A. (2013). *Aggregation-induced emission: fundamentals and Applications*. John Wiley & Sons.

Rettig, W. (1986). Charge separation in excited states of decoupled systems-TICT compounds and implications regarding the development of new laser dyes and the primary process of vision and photosynthesis. *Angewante Chemie International Edition*, Vol. 25, pp. 971-988.

van Walree, C. A., Kaats-Richters, V. E. M., Veen, S. J., Wieczorek, B., van der Wiel, J. H., and van der Wiel, B. C. (2004). Charge-transfer interactions in 4-donor 4′-acceptor substituted 1,1-diphenylethenes. *European Journal of Organic Chemistry*, Vol. 2004, pp. 3046-3056.

Wakefield, B. J. (1995). *Organomagnesium methods in organic synthesis*. Academic Press.

Walker, R., Audorff, H., Kador, L., and Schmidt, H. W. (2009). Synthesis and structure–property relations of a series of photochromic molecular glasses for controlled and efficient formation of surface relief nanostructures. *Advanced Functional Materials*, Vol. 19, pp. 2630-2638.

Yanagisawa, A. and Yoshida, K. (2011). Recent advances in selective reactions promoted by barium reagents. *Synlett*, Vol. 2011, pp. 2929-2938.

Yanagisawa, A., Yamafuji, S., and Sawae, T. (2016). α-Selective allylation of isatin imines using metallic barium. *Synlett*, Vol. 2016, pp. 2019-2023.

Zúñiga-Núñez, D., Zamora, R. A., Barrias, P., Tirapegui, C., Poblete, H., Cárdenas-Jirón, G., Alarcon, E. I., and Aspée, A. (2018). Theoretical rationalisation of the photophysics of a TICT excited state of cinnamoyl-coumarin derivatives in homogeneous and biological membrane models. *Physical Chemistry Chemical Physics*, Vol. 2018, pp. 27621-27629.

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