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Regioselective Synthesis of Tetraphenyl-1,3-butadienes with Aggregation-Induced Emission

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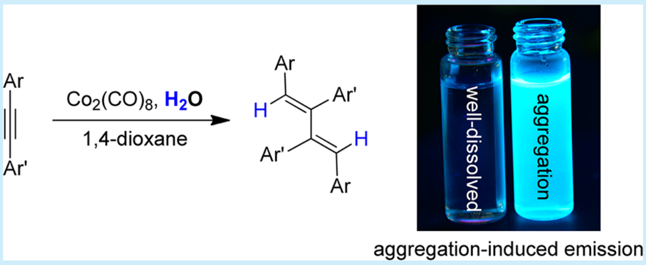
S *Supporting Information*

ABSTRACT: In the presence of substoichiometric amounts of $Co_2(CO)_8$, internal bisarylalkynes undergo reductive dimerization with good to excellent yields. The $Co_2(CO)_8$-induced reactions described are experimentally quite simple and provide a very useful synthetic procedure for the synthesis of tetraphenylbutadienes which exhibit aggregation-induced emission enhancement, i.e., weak emission in good solvents but strong fluorescence in solvents that lead toward formation of aggregates or in the solid state.



The past decade has seen an exponential increase in the design and exploration of efficient luminophoric materials for various potential applications including the fluorescent biological labels, organic light-emitting diodes (OLED), and optical sensors.[1] However, many conjugated organic emitters are strongly emissive in solution but lose their emission in the solid state through the notorious photophysical effect of aggregation-caused quenching due to energy transfer and the formation of excimers.[2] Because fluorescent materials in organic devices are normally functioning in the solid film state, development of efficient conjugated luminophores with enhanced film emission is of particular interest. Tang and co-workers have reported several materials that exhibit a unique phenomenon named aggregation-induced emission (AIE).[3] Such molecules were nonemissive in dilute solutions but became strongly emissive upon aggregation. Since then, a large number of AIE-active luminophores including silole,[4] tetraphenylethylene (TPE),[5] triphenylethylene,[6] cyanostilbene,[7] azobenzene,[8] anthacene-based imidazolium salt,[9] triarylamine,[10] and metallole[11] derivatives have been developed by various research groups. This AIE process may generally be attributed by several mechanisms including restriction of intramolecular rotation, formation of J-aggregates, intramolecular planarization, dual mode of assembly, inhibition of photoisomerization, and photocyclization.[3a,b,7a,12] However, the effect of molecular structure and packing arrangement has rarely been investigated, although the structure−property relationship is of great value in terms of gaining new insights into the development of new AIE luminogens. On the basis of these considerations, it is envisioned that extending π-conjugation of TPE to butadienes incorporating sterically demanding substituents shall lead to new AIE luminogens with multiple sites for structural modifications which enable facile emission color tuning. Moreover, conjugated dienes are one of the most important scaffolds to increase molecular complexity in organic synthesis.[13] Generally, linear dienes such as **A** can be synthesized easily,[14] whereas the synthesis of branched dienes such as **B** is more cumbersome (Figure 1).[15] Hence, the regioselective formation of branched dienes is a highly challenging task. Recently, branched dienes have been synthesized by Ru-hydride catalyzed dienyl isomerization,[16] alkaline desilation of 2,5-bis(*para*-monosubstituted phenyl)-siloles.[17] Using a stoichiometric amount of Cp_2Zr (obtained through in situ reduction of Cp_2ZrCl_2 with a "mischmetall" lanthanide alloy) resulted in the formation of branched dienes along with rearranged products.[18] However, selective formation of branched diene is limited success. Among various types of transition-metal catalysts, cobalt has been employed as a highly reactive catalyst for the carbon−carbon bond-forming reactions by Oshima,[19] Knochel,[20] Gosmini,[21] and others.[22]

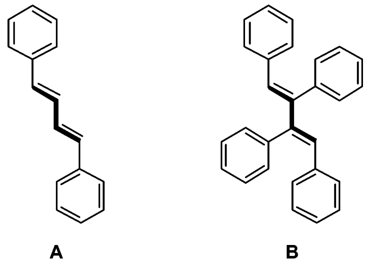


Figure 1. Linear (**A**) and branched dienes (**B**).

Cobalt complexes have been extensively used for alkyne trimerization in anhydrous conditions.[22] Herein, attempts to carry out a dicobaltoctacarbonyl-catalyzed cyclotrimerization of internal bisarylethynes in the presence of water has led to the formation of branched dienes. To the best of our knowledge, this is the first report of cobalt-mediated intramolecular alkyne self-coupling for the synthesis of branched 1,3-dienes. This novel cobalt-mediated one-pot method for the reductive dimerization

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of internal alkynes under mild conditions in the presence of water is described (Figure 2).

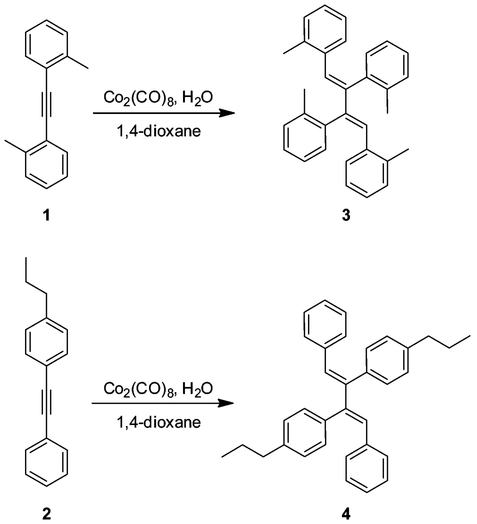


Figure 2. Synthesis of tetratolylbutadiene (**3**) and dipropylphenyl diphenylbutadiene (**4**).

Optimal conditions for the dimerization of the alkynes were found through a series of screening experiments in which amounts of the dicobalt catalyst and water and the choice of solvent were all found to have a profound effect on the reaction yield. In addition, the AIE effect of compounds **3** and **4** was tested by blending water with acetonitrile in different ratios.

In the initial trial, diphenylethynes (**1** and **2**) were stirred with 1 mol % of $Co_2(CO)_8$ and 2 equiv of H_2O in 1,4-dioxane to afford 1,3-dienes (**3** and **4**) in low yield (entry 1, Table 1). With increasing mol % of $Co_2(CO)_8$, yields steadily increased until a maximum yield of 60%, accompanied by 25% of unreacted starting diphenylethyne, was reached with a 20 mol % loading of the cobalt reagent (entries 2–5, Table 1). A trace amount of trimerization product, hexaphenylbenzene (HPB), was also detected by NMR spectroscopy. No additional increase in yield was observed upon further increasing the load of $Co_2(CO)_8$ (entries 6 and 7, Table 1). Addition of 2 equiv of water is vital for the formation of the butadiene product. In the complete absence and also with a large excess of water, the reaction was inhibited (entry 8, Table 1). The use of other solvents, such as acetonitrile, dimethylformamide, and *o*-xylene, was also found to be effective but resulted in lower yields (entries 9–11, Table 1).

Table 1. Optimization of Reaction Conditions for Preparing 3 and 4[a]

			yield (%)	
entry	$Co_2(CO)_8$ (mol %)	solvent	3	4
1	1	1,4-dioxane	18	11
2	5	1,4-dioxane	25	20
3	10	1,4-dioxane	36	39
4	15	1,4-dioxane	49	45
5	20	1,4-dioxane	60	58
6	25	1,4-dioxane	54	56
7	30	1,4-dioxane	55	50
8	20	1,4-dioxane	0[b,c]	0[b,c]
9	20	acetonitrile	22	24
10	20	dimethylformamide	10	12
11	20	*o*-xylene	26	20

[a] A mixture of alkyne **1** or **2** (1.0 mmol), $Co_2(CO)_8$ (20 mol %), and H_2O (2.0 mmol) in a solvent (4 mL) was heated to reflux at 110 °C for 18 h. [b] In the absence of water. [c] 10 mmol of H_2O was added.

The structures of the products were deduced from their elemental analysis data, mass, ^1H NMR, and ^{13}C NMR spectra. The molecular structure of the dimer **3** was confirmed by single-crystal X-ray analysis. As shown in Figure 3, the transoid butadiene skeleton in compound **3** is coplanar with the dihedral angle of 180° of the butadienyl unit, and the four phenyl rings are twisted out of the diene plane with dihedral angles of 44.1° and 80.9°. Figure 4 shows CH⋯π interactions, 2.85 and 2.71 Å, respectively, in the *bc*-plane.

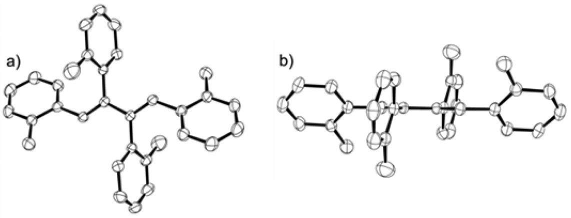


Figure 3. ORTEP representations of tetratolylbutadiene (**3**) with 30% probability level. Hydrogen atoms are omitted for clarity: (a) top and (b) side views.

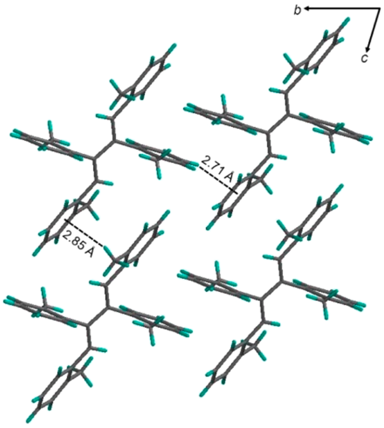
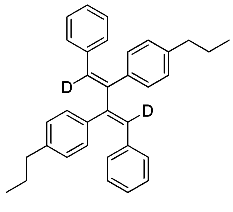
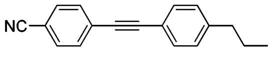


Figure 4. Molecular packing diagram of **3** showing C–H–π interactions viewed along the *bc*-plane.

To better understand the role of water and cobalt reagent and to help elucidate the mechanism of the reaction, an isotopic-labeling experiment for the dimerization of internal alkyne **2** by the addition of D_2O instead of H_2O was performed. Analysis of the product **4′** by ^1H NMR shows that both olefinic protons of the diene were deuterated. This confirms the origin of the hydrogen atoms as being from the water molecules.



4′



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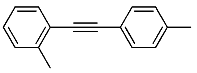

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A plausible reaction mechanism for the reductive dimerization reaction is proposed (Figure 5) that closely follows the suggested mechanisms for $Co_2(CO)_8$-catalyzed cyclotrimerization and oligomerization reactions.[23] Intermediate **I** is derived by addition of one molecule of alkyne via its π-system to $Co_2(CO)_8$ under loss of two molecules of carbon monoxide. The thus π-coordinated alkyne is activated for oxidative addition to the Co atoms and coupling with another alkyne molecule once this second alkyne enters the coordination sphere of the Co cluster. Space at the Co-cluster for the second alkyne to enter is made available by dissoication of at least one other carbon monoxide molecule. Once both alkyne molecules are π-coordinated to the Co-cluster, they couple, and at the same time, the diene that is formed oxidatively couples to one of the Co atoms to form the cobaltacyclopentadiene intermediate **II**.[24] Cleavage by water releases the dienes and oxidized cobalt reagent. The observed stoichiometry and the deuterium-labeling experiments thus confirm the above mechanism as a redox reaction of the cobaltacyclopentadiene intermediate **II** with water under formation of the butadiene product and an oxidized cobalt(II) byproduct.

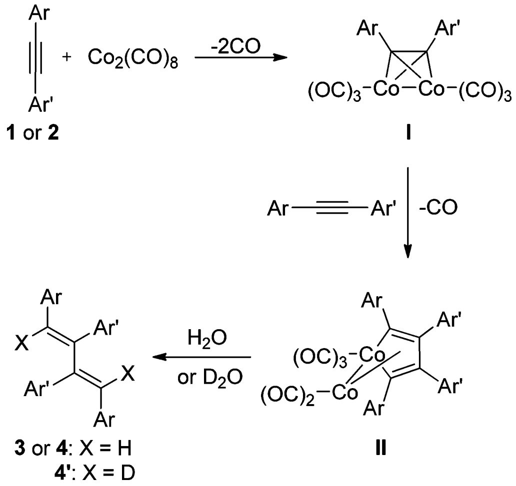

Figure 5. Proposed mechanism for the formation of **3**, **4**, and **4′**.

For **1**, the sterics from the *o*-CH_3 may have assisted the formation of dimer **2** by quenching the trimerization with H_2O. However, the steric factor was removed in **3** which also yielded dimer **4** in a moderate yield. Moreover, regioselectivity for the formation of **4** was achieved, which was suspected to be electronically controlled. The same reaction conditions on **5** with an electron-withdrawing cyano end did not yield the butadiene product with recovery of most of the starting compound. For **6**, the reaction afforded an inseparable mixture of isomeric dimers in 69% yield with recovery of 20% of the starting compound. The sterics do not lead to regioselectivity. More examples are needed to elucidate the detailed mechanism.

It is pertinent to mention here that compared to 1,1,4,4-tetraphenylbutadiene, a typical blue emitter, derivatives of tetraphenylbutadiene are normally not regarded as fluorescent materials in solution.[25] The fluorescence of *o*-tolyl derivative **3**, for example, is very faint in organic solvents such as acetone, THF, and acetonitrile. This changes if molecules of **3** are induced to aggregate. The addition of water to an acetonitrile solution of **3**, for example, induces the aggregates thus formed to emit blue light with a maximum at 390 nm, indicating that **3** is AIE active.

As an example, emission spectra of **3** in water/acetonitrile are shown in Figure 6. In the absence of water, solutions of **3** and **4** in acetonitrile are hardly fluorescent upon irradiation with UV light. This may be ascribed to intramolecular rotation of phenyl groups in solutions, which results in vibronic coupling and radiationless decay of the excited states in solution. The effect of water on the fluorescence was evaluated through measurement of fluorescence spectra of **3** and **4** in a mixed solvent of water and acetonitrile. The fluorescence quantum yield Φ_{em} of the acetonitrile solution is as low as 0.001. The Φ_{em} is almost unchanged upon addition of water up to 40 vol % but starts to sharply increase with higher water fraction (f_w). When the volume fraction of water is increased to 90 vol %, Φ_{em} rises to 0.83 and 0.87 for compounds **3** and **4**, which are about 800 times higher than that of the acetonitrile solution and 3 times higher than that of unsubstituted tetraphenylbutadiene core.[26]

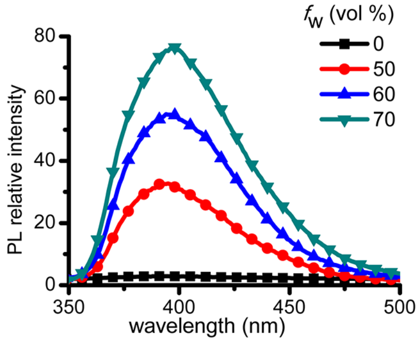

Figure 6. Emission spectra of **3** in water/acetonitrile solvent mixtures with different volume percents of water (0, 50, 60, and 70 vol % of water in acetonitrile). Concentration of **3**: 10 μM.

The trajectory of the Φ_{em} change suggests that molecules of **3** start to aggregate significantly at a water fraction of >50 vol % (Figure 7). As water was a poor solvent for **3**, increasing the water vol % of the water/acetonitrile solvent system induced aggregation of **3**.

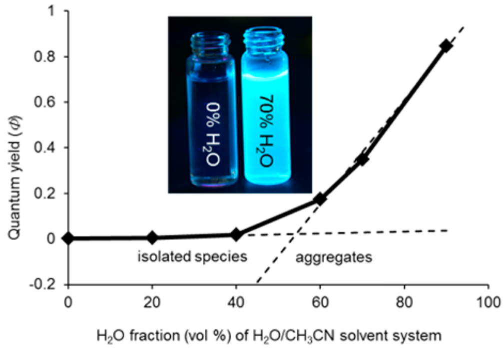

Figure 7. Photoluminescence quantum yields of **3** vs solvent composition of the water/acetonitrile mixture. The inset shows the photographs of **3** in acetonitrile with 0 and 70 vol % of water.

In summary, a facile, mild, and highly regioselective synthesis of branched 1,3-dienes is described through a cobalt-mediated reductive-coupling of internal arylalkynes. In view of the readily available starting materials, simple operation of the process, as well as high regioselectivity, this methodology may become a useful tool for the synthesis of dibranched 1,3-butadienes. The fluorescence switching behavior of tetraphenylbutadiene with sterically demanding substrates suggests that aggregation-induced emission is caused by restricted intermolecular rotation of the phenyl groups. Our ongoing research is directed toward development of highly fluorescent organic solids based on the molecular design of the present study.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental procedure and full characterization of new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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