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## Electrochemiluminescence Platforms Based on Small Water-Insoluble Organic Molecules for Ultrasensitive Aqueous-Phase Detection

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Abstract: The achievement of highly efficient detection in aqueous phase for water-insoluble organic molecule probes is highly challenging. In this study, we discovered the bright aggregated state electrochemiluminescence (ECL) of 1,1-disubstituted 2,3,4,5tetraphenylsiloles by a co-reactant approach, and we constructed a heterogeneously aggregation-induced emission ECL (HAIE-ECL) at the electrode surface that showed very high ECL efficiency (37.8%) and the selective recognition for the industrially important DNBP plasticizer with a lower detection limit of 0.15 nM in the water phase. The mechanism study indicates that the ECL is mainly generated due to the high electron affinity of siloles and restriction of the intramolecular motions caused by their propeller-like noncoplanar structures. The new system realizes for the first time the sensing of organic-based ECL in the water phase by solving the crucial problems of water-insolubility and aggregation-caused quenching (ACQ), and demonstrate potential for further application because of its design and high efficiency.

Organic light-emitting probes play a highly significant role in the field of medical research, life sciences, and environmental analysis.<sup>[1]</sup> However, the probes' application in an aqueous phase is limited due to the water insolubility for most of these probes. Electrochemiluminescence (ECL) is an electrochemical activation of suitable luminophoregenerating species at the electrode surface that then undergo electron-transfer reactions to form excited states that emit light.<sup>[2]</sup> ECL also provides a solution for the detection in an aqueous phase by modifying the waterinsoluble organic-based luminophores at the surface of electrodes to form the heterogeneous system. In fact, ECL is an analytical method combining chemiluminescence and electrochemical technologies with the advantages of high sensitivity, simple instrumentation, fast analysis, stable reagents, and easy control on light emission.<sup>[2,3]</sup> Hence ECL has been widely used in the detection of medicine, water, food and immune systems in recent years.<sup>[2,4]</sup> Based on the luminophores, ECL systems are mainly classified

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into three types, namely, inorganic systems<sup>[2b,5]</sup>, organic systems<sup>[2b,6]</sup>, and nanomaterial systems<sup>[2b,7]</sup>.

In most cases, the direct modification of ECL at the electrode surface to luminophores form heterogeneous ECL (HECL)<sup>[8]</sup>, where the emitters are confined at the electrode surface, is simple, convenient, high-resolution, has low interference to analytes<sup>[9]</sup> and is particularly suitable for water-insoluble ECL luminophores. luminophores Organic-based are regarded as optimal candidates for HECL due to their lack of metal content, high activity, water-insolubility, and inherent capability for the fine-tuning of their emission wavelengths. However, studies on HECL are rare because aggregationcaused quenching (ACQ) of light emissions observed for many organic luminophores in the aggregated state tend to hamper their optical performances due to intermolecular  $\pi$  $-\pi$  stacking.<sup>[10]</sup> Hence the development of organic-based luminophores that can intensely emit light in the solid state will contribute to solve the problem.

Silacyclopentadienes (Siloles) show unique chemical and optical properties due to their low-lying LUMO levels because of the electronic interaction between the  $\pi$  \* orbital of the butadiene moiety and the  $\sigma^*$  orbital of the exocyclic Si-R bond.<sup>[11]</sup> Based on the research of siloles, (AIE) the novel aggregation-induced emission phenomenon was discovered by Tang and coworkers.<sup>[12]</sup> However, only a small number of studies have been investigated the ECL of siloles. Bard<sup>[13a]</sup> and Ding<sup>[13b]</sup> groups reported the efficient and stable ECL of 2,5arylethynyl and 2,5-thienyl disubstituted siloles. respectively. Nevertheless, these ECLs did not use the unique AIE characteristic of siloles and were obtained in homogeneous organic solvents such that their detection in aqueous phase was limited.



Scheme 1. Chemical structures of 1,1-disubstituted 2,3,4,5-tetraphenylsiloles and 1,1-dimethyl-3,4-diphenyl-2,5-bis(trimethylsilyl)silole

1,1'-Disubstituted 2,3,4,5-tetraphenylsiloles (Scheme 1), such as 1,1'-dimethyl-2,3,4,5-tetraphenylsilole (**DMTPS**), 1methyl-1,2,3,4,5-pentaphenylsilole (**MPPS**) and 1,1,2,3,4,5hexaphenylsilole (**HPS**), can be synthesized in a facile manner and are structurally simple, non-toxic, highly stable and are the

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archetypes of AIE molecules<sup>[12]</sup> that are either weakly fluorescent or non-fluorescent in solution but are strongly fluorescent in the aggregated state<sup>[14]</sup> (Figure S6). To the best of our knowledge, their ECLs have not been observed to date. This finding also indicates that siloles are superior for forming tightly aggregated films at the electrode surface (Figure S7) because silicon-based materials exhibit strong affinity with electrodes due to the interaction between the silicon atoms and oxygen functional groups on the glassy carbon electrodes<sup>[15]</sup>. So we can modify the above siloles at the electrode surface to form stable heterogeneous ECL systems.

First, we investigated the annihilation HECL of these siloles under the electrochemical conditions (a wide potential window of -2 V to 2 V (vs Ag/Ag<sup>+</sup>), 0.1 V/s scan rate, 0.1 M PBS, and 7.5 pH). Unfortunately, no ECL signals could be obtained. It was reported that co-reactants, such as oxalate ion  $(C_2O_4^{2-}),$ tri-n-propylamine (TprA) and potassium persulfate (K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>), could produce an intermediate that could react with an ECL luminophore to produce an excited state and generate significant ECL.<sup>[2b,2c]</sup> Considering the high electron affinity of siloles,<sup>[11]</sup> we selected K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> as the coreactants, and finally, excellent cathodic HECL emissions could be obtained. The results show that the substituents at 1,1position have a strong effect on the ECL emissions, and the intensities were in the order (DMTPS)<MPPS<(HPS) (Figure 1A). This finding may be observed because aromatic substituents at 1,1-positions effectively enhance higher  $\sigma^* - \pi^*$  conjugation interactions between exocyclic carbon atoms and endocyclic silicon atom that result in their more low-lying LUMOs and higher electron affinities than that of alkyl substituents, and larger substituents at the 1,1-positions enhances the steric hindrance to restrict the rotation of the

phenyl groups at the silole ring, reducing the loss of energy caused by the intermolecular interaction, and then increases the ECL efficiency in the aggregated state.<sup>[14]</sup> By contrast, to further explain such aggregation-induced ECL, the ECLs of these silole monomers in homogeneous organic solvents were also investigated, but the observed signals were very weak and decreased to approximately one twentieth of the signals on the bare electrode (from 3000 to 150 a.u. Figures 1B). This result indicates that 1,1-disubstituted 2,3,4,5-tetraphenylsiloles exhibit high ECL emissions in the aggregation state and weak emissions in solution which, by analogy to fluorescence, is called aggregation-induced emission (AIE). Owing to the unique propeller-like noncoplanar structure of siloles (Figure S9), aggregations effectively reduce the nonradiative energy decay by suppressing intramolecular motions and are largely responsible for the generation of such ECL emissions.

2.5-Substituents have the strongest effects on the electronic and optical properties of siloles<sup>[11]</sup>. Silvl-substituents exert large steric effects and unique electronic effects. Therefore, we synthesized 2,5-bis(trimethylsilyl)-substituted silole (DTMPS) (Scheme S2) that which shows different UVvis absorption (Figure S5) and very little aggregate-state fluorescence emission at the electrode surface because trimethylsilyl groups (-SiMe<sub>3</sub>) are not the chromophores and destroy the conjugation between 2,5-positons and core silole ring (Figures S6 and S7). When DTMPS was tested with K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> as a co-reactant under the same conditions, the ECL intensity was fairly low and was only 1/30 (100 vs 3000) of the 1,1'-disubstituted intensity observed for 2,3,4,5tetraphenylsiloles (Figures 1C). This finding indicates that phenyl-substituents at the 2,5-position are indispensable for generating such ECL.



Figure 1. ECL intensities vs. different siloles/K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> systems: **A**. Siloles in the aggregated state modified at the electrode surface under the conditions of a potential window of -1.6 V to 0 V (vs Ag/Ag<sup>+</sup>), scan rate of 0.1 V/s, 0.1 M PBS containing 0.1 M KCl and 0.1 M K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>, and pH 7.5, **B**. 10 mM silole in 80% dimethyl sulfoxide (DMSO)/H<sub>2</sub>O solution under the same conditions as **A**; **C**. ECL intensity vs. potential: a. **HPS** + K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>, b. **MPPS** + K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>, c. **DMTPS** + K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>, d. **DTMPS** + K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>, e. K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> under the same conditions as **A**.

SEM images of four silole aggregates modified on glassy carbon electrodes show that AIE-active silole aggregates (HPS, DMTPS and DMTPS) exhibit apparent torispherical structures (Figure S8A, B, C), while non-AIEactive DTMPS aggregates were found in the form of ribbons (Figure S8D). This may be due to the excellent solubility of DTMPS in THF benefiting from trimethylsilylsubstituents. These results revealed that AIE-active silole aggregates provided higher surface area than the non-AIEactive molecular aggregates to the working electrodes and have a positive effect on their ECL behaviours.

Theoretical density functional theory (DFT) calculations were carried to obtain the electronic structures of the siloles at the B3LYP/6-31G(d) level of theory (Figure S9). The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) for the three

1,1-disubstituted siloles are qualitatively similar. The LUMOs mainly arise from the  $\sigma^* - \pi^*$  interaction between the  $\sigma^*$  orbital of the exocyclic  $\sigma$  bonds on the silicon atom and the  $\pi^*$  orbital of the butadiene group, giving rise to their lower-lying LUMO levels and readily available electrons. The band energy gaps between HOMO and LUMO for the three 1,1-disubstituted siloles are similar and are directly proportional to their ECL intensities, while non-ECL-active **DTMPS** exhibits comparatively higher LUMO and lower HOMO energy levels and therefore a larger energy gap (Figure S10), this may be due to that trimethylsilyl groups (-SiMe<sub>3</sub>) suspend the conjugation between 2,5-positons and core silole ring and the  $\sigma^* - \pi^*$  electronic interaction is obviously weakened. The results suggest that ECL intensities are closely related to the HOMO and LUMO energy levels, providing an approach for understanding the ECL emission mechanism. Meanwhile, HPS with a low-lying LUMO level and smaller HOMO-LUMO band gap showed the strongest ECL emission and was selected as the optimal ECL luminophore. The influence factors such as the pH, scan rate, and concentrations of HPS and K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> were optimized to obtain the best experimental conditions for the HPS/K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> ECL system (a potential window of -1.6 V to 0 V (Vs Ag/AgCl), scan rate of 0.1 V/s, 0.1 M PBS containing 0.1 M KCl and 0.1 M  $K_2S_2O_8$ , pH 7.5, and HPS concentration of 14.0 mM) for further study (Figure S16).



Figure 2 A. (a) Normalized PL spectrum of HPS in the solid state, (b) HAIE-ECL spectrum of the HPS/K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> system; B. CV waves for the K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> (blue line), HPS aggregates (red line) and the mixture of the HPS + K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> (black line)

Figure 2A shows the ECL spectrum for HPS/K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> system with a maximum at 504 nm, which is very similar to the photoluminescence (PL) spectrum that has a maximum at 500 nm (Figure S6). Good agreement between the ECL and PL spectra revealed the ECL undergoes a similar process to PL from the excited state of HPS to its ground state, emitting light. The ECL efficiency of HPS/K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> to the Ru(bpy)<sub>3</sub><sup>2+</sup>/TPrA system was calculated to be 37.8%, and is one of the higher value obtained to date<sup>[2,6]</sup>. Figure S11 presents the ECL stability of the HPS/K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> system under consecutive cyclic potential scans for 17 cycles in the buffer. The cathode ECL intensity showed good stability with a relative standard deviation of 1.24%, making it reliable and reversible as a novel ECL sensor.

The reduction CV peak of the aggregated HPS was observed at -0.83 V (Figure 2B) and is close the peak of the monomers in the DCM solution (-0.76 V in Figure S12). The

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reduction peak changed obviously from -0.83 to -1.3 V after mixing HPS and K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> (Figure 2B). It was reported that siloles can be reduced to form the corresponding silole radical anions<sup>[16]</sup>. Therefore, the following possible mechanism was proposed: first, HPS obtained an electron to generate HPS radical anion. Then, the reaction between the silole radical anions and S<sub>2</sub>O<sub>8</sub><sup>2-</sup> produced the SO<sub>4</sub><sup>--</sup> strong oxidant species (Figure 3). In the corresponding cyclic voltammogram, an obvious irreversible reduction peak at approximately -1.3 V is attributed to the electrochemical reduction between the HPS radical anions and S2O82-. Following the electron transfer between the silole radical anions and the SO4<sup>--</sup> strong oxidant species, excited siloles formed and immediately returned to the ground state through light emission. On the other hand, intramolecular motions (RIM) of the AIE-active HPS was restricted due to the spatial constraint in the aggregate state that contributed to prevent the nonradiative decay<sup>[14]</sup> and enhance the ECL intensity. Thus, both the co-reactant and AIE effect made significant contributions to the ECL performance.

(1)	HPS + e⁻ → HPS '¯
(2)	HPS $^{-}$ + S <sub>2</sub> O <sub>8</sub> <sup>2-</sup> $\longrightarrow$ HPS + SO <sub>4</sub> <sup>2-</sup> + SO <sub>4</sub> <sup>-</sup>
(3)	HPS $\cdot$ + SO <sub>4</sub> $\cdot$ + HPS *
(4)	HPS * $\longrightarrow$ HPS + $hv$

Figure. 3 Proposed ECL mechanism for the HPS/K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> system.

Plasticizers are organic phthalate compounds from the production of plastics to improve the mechanical and antioxidant properties. However, the structure of plasticizers is similar to the hormones found in biological organisms and therefore, plasticizers are known as "environmental hormone";<sup>[17]</sup> they may cause abnormalities in the reproductive system and even the risk of malformation and cancer.<sup>[18]</sup> Currently, plasticizers are widely found in all areas of daily life and have become the most serious organic pollutants worldwide.

It was noted that silole anions can effectively undergo electron transfer reactions to the carbonyl compounds (Scheme 2)<sup>[19]</sup>. To verify the application of the **HPS**/K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> ECL system, the detection of di-n-butyl ortho-phthalate phthalate (**DNBP**) as a representative industrial plasticizer that is derived from plastic catalysts used as electron donors<sup>[20]</sup> and post-processing of plastics was performed in this study.



Scheme 2. Example of silole electron transfer reactions

Plasticizers are mainly detected by chromatography and chromatography-mass spectrometry.<sup>[21]</sup> Owing to the issues of volatilization, instability, and low plasticizer content, the existing methods have some shortcomings such as a poor separation for compounds with similar polarities, the difficulties in the choice of the solvent and fixed phase, and low sensitivity. ECL analysis has been proven to be highly selective and sensitive and may avoid the analytical shortcomings described above.<sup>[2,4]</sup>

The HPS/K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> ECL system can also produce the excited state intermediates: silole radical anions that could be quenched by an ester: DNBP via electron transfer reactions<sup>[19]</sup> (Scheme 2). As shown in Figure S17, the ECL intensity decreased linearly when DNBP was added to the HPS/K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> system, suggesting a potential application of the ECL system to the sensing of DNBP. Figure S18 shows a linear correlation between the decrease in the cathodic ECL intensity and increase in the DNBP concentration in the range of the plot of  $ln(l_0/l)$  versus the **DNBP** concentration, where  $l_0$  and l represent the ECL intensities in the absence and presence of **DNBP**, respectively. The linear range was 5 ~ 2500 nM and the limit of detection was 0.15 nM (S/N = 3), with a good correlation coefficient  $R_2 = 0.9946$  (n = 3). To demonstrate the selectivity, we examined the effect of other plastic residues (Mg2+, Al3+, Cl-, Ti<sup>4+</sup> and phenols)<sup>[19]</sup>. The results are shown in Figure S19, and it is clear that only **DNBP** responded to the **HPS**/K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> system. This may be due to the electron transfer of the silole intermediate radical anions being very specific to the carbonyl compounds (Figure S20). The new analysis method was very sensitive and selective for the detection of DNBP compared to other methods reported including traditional the chromatography and electrochemical analysis method to date (Table S2).[22]

In summary, we developed a facile and feasible silole/K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> ECL system named HAIE-ECL. Both experiments and theoretical calculations revealed the inherently electronic and non-coplanar structure of this system, and it was shown that the HOMO and LUMO levels of the system affected by the substituents at 2,5 and 1,1-postions played the dominant role in the HAIE-ECL emissions. The new system is simple design, convenient to use, environment friendly, low interference to analytes, and the detection of the widely used DNBP industrial plasticizer by the  $HPS/K_2S_2O_8$  ECL system showed high sensitivity and selectivity. This work not only introduced AIE luminophores for the first time to solve the water-insolubility and aggregation-caused quenching (ACQ) problems found for organic-based molecule probe systems but also established a highly efficient electrochemical method for analysis of the DNBP industrial plasticizer.

#### **Experimental Section**

Experimental details are available in the online supporting information.

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## **Keywords:** electrochemiluminescence • siloles • heterogeneous • aggregation-induced • plasticizer

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Layout 1:

#### COMMUNICATION

A novel heterogeneously aggregationinduced emission electrochemiluminescence (HAIE-ECL) system with high ECL efficiency has been developed according to AIE strategy. The new system can achieved the detection of а widely existed plasticizer: DNBP in water phase, and solve waterinsolubility and aggregation-caused quenching (ACQ) lying in the small organic molecule probe systems



Z. Han, Y. Zhang, Z. Yang, H. Sun, Y. Xu, X. Ma, D. Shan, J. Chen, S. H, Z. Zhang, X. Lu\*

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Electrochemiluminescence Platforms Based on Small Water-Insoluble Organic Molecules for Ultrasensitive Aqueous-Phase Detection