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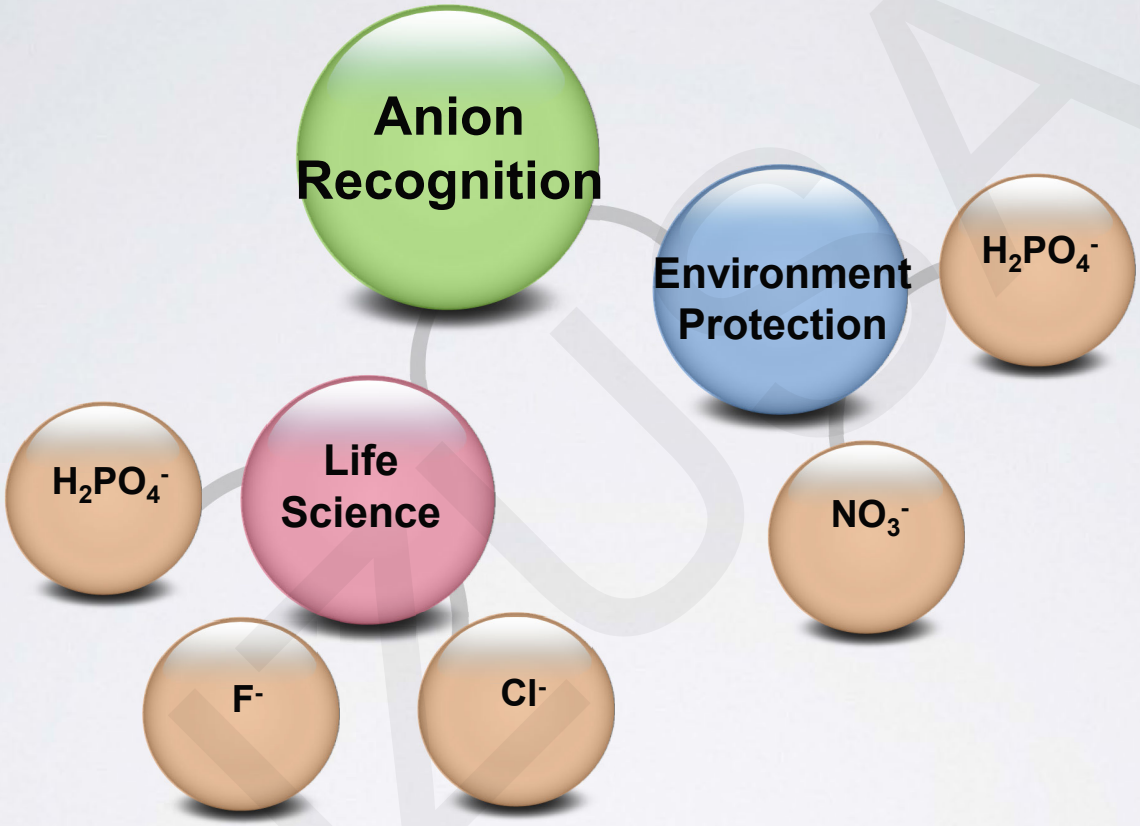
Synthesis of ferrocene- and azobenzene-based compounds for anion recognition

Key words:

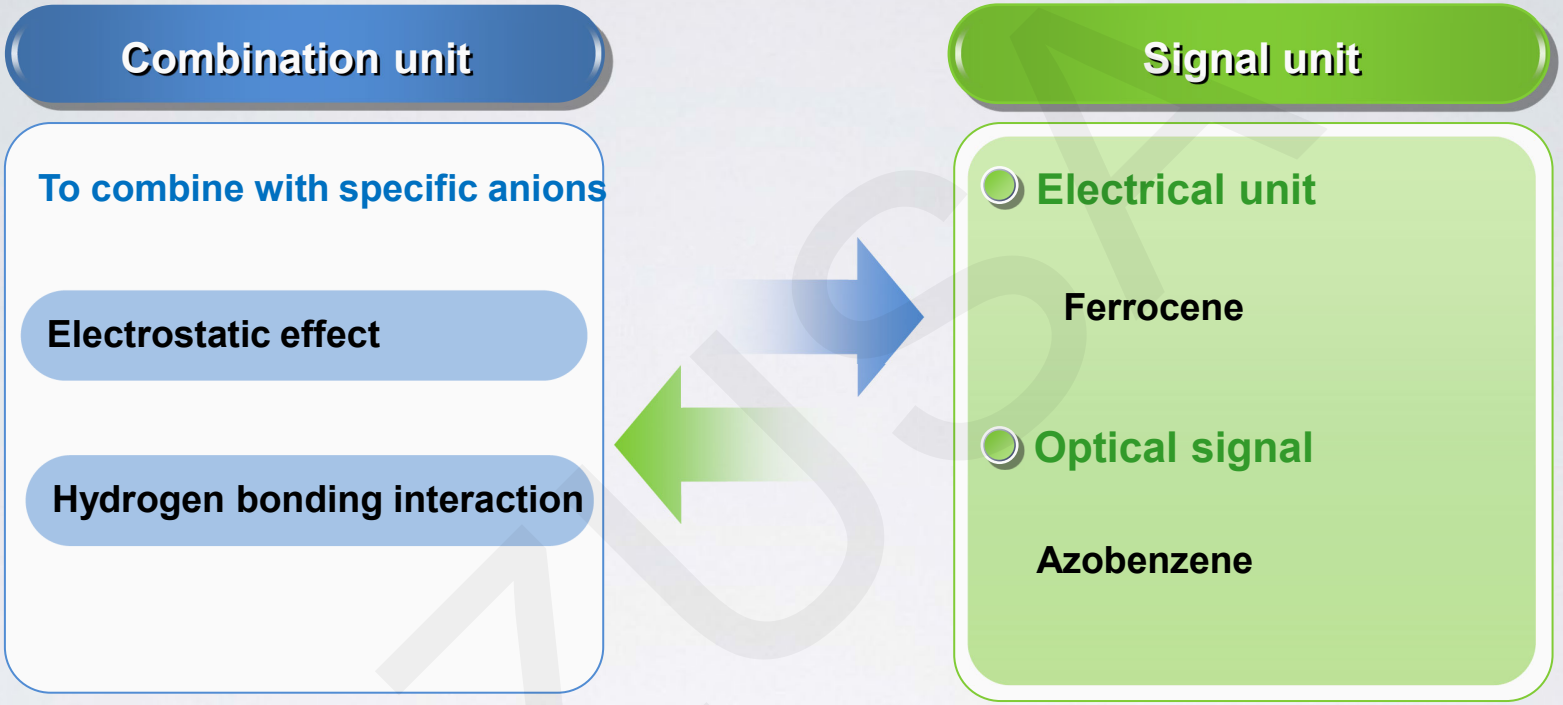
Ferrocene; Azobenzene; Hydrogen bonding; Anion recognition

Significance of anion recognition



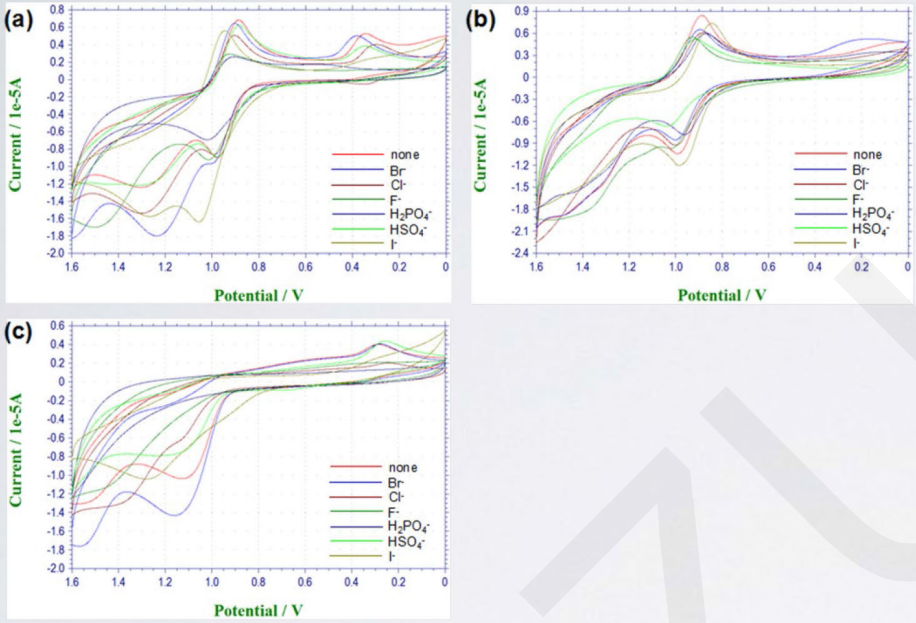
Excess F^- and $H_2PO_4^-$ will harm the environment, the ecological balance and people's health (Chao Li *et al.*, 2014).

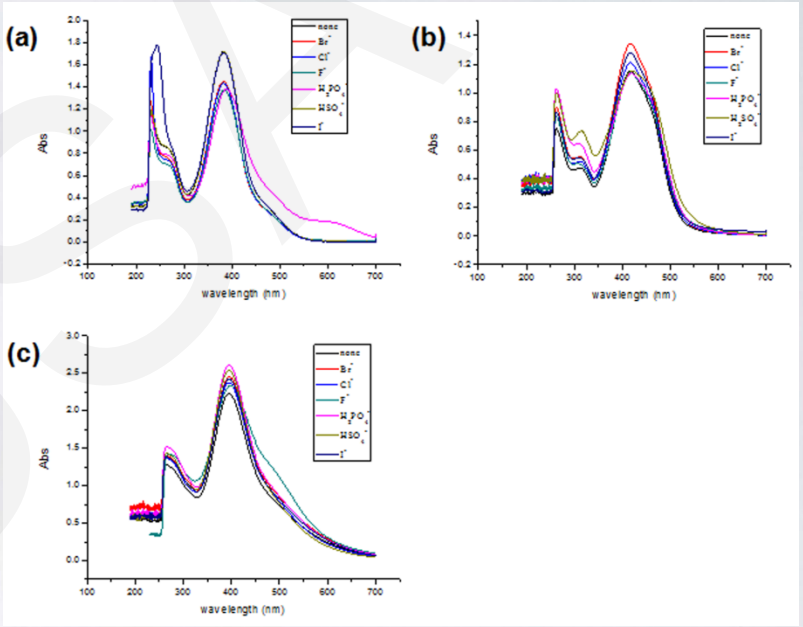
Composition of recognition molecules



Anion recognition material is usually composed of two parts, which are the combination unit and the signal unit. The combination unit is mainly used for the combination of anions, while the signal unit is used to transmit the binding information through a certain way.

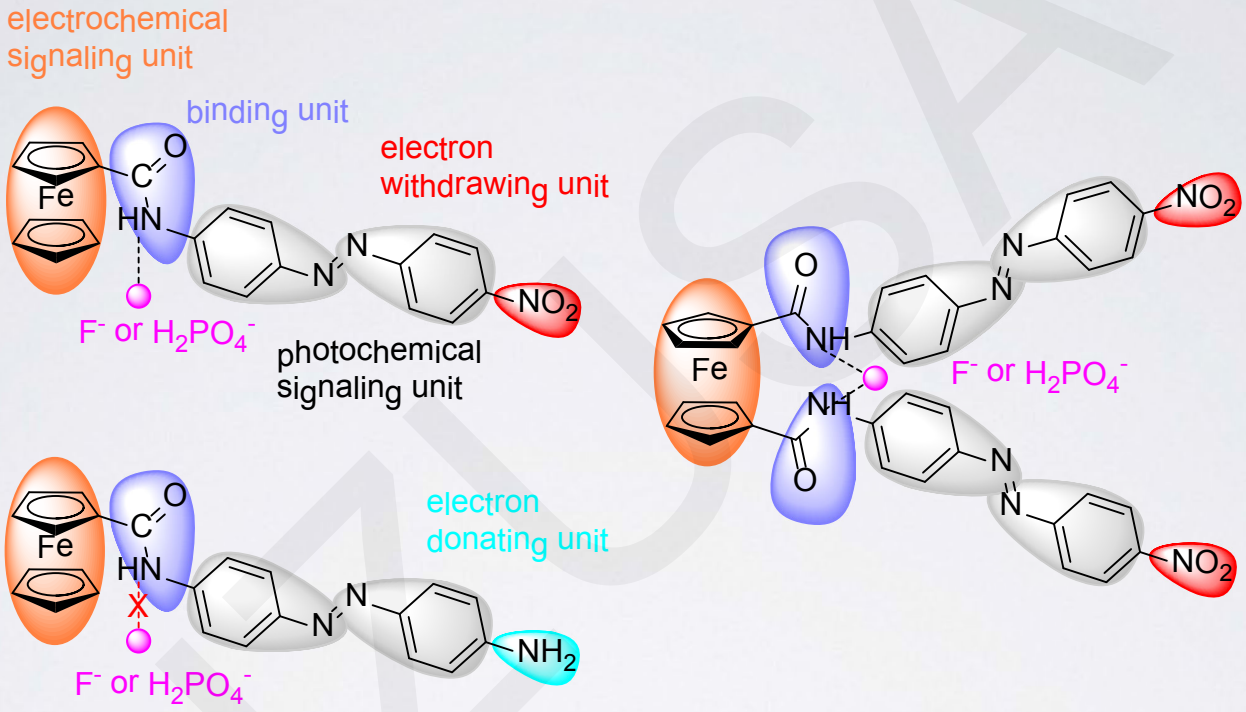
Anion recognition behavior of the synthesized compounds





UV–Vis absorption spectroscopy (UV) and cyclic voltammetry (CV) were applied to study the anion recognition behavior of the synthesized compounds. The results showed that a nitro group substituent has a positive effect on the binding affinity and sensitivity, while an amino group substituent has a negative effect on the sensitivity.

Plausible mechanism of the anion recognition processes



Nitro group can cause an obvious charge transfer which will result in an intensity sharpening of the hydrogen-bonding interaction. However, amino group's electro effect will weaken the hydrogen bonding.

Conclusions

Three ferrocene- and azobenzene-based compounds linked with an acyl amino group were successfully synthesized. The anion recognition behaviors of the synthesized ferrocenyl azobenzenes with specific guest anions based on hydrogen bonding were studied by electro- and photo-chemical techniques. The results showed that ferrocenyl azobenzene **1** and ferrocenyl azobenzene **3** exhibited high binding affinity and sensitivity for F^- and $H_2PO_4^-$, while ferrocenyl azobenzene **2** was not sensitive to F^- and $H_2PO_4^-$, as little change could be observed in the absorption spectrum or by naked-eye detection. These interesting phenomena may well be caused by the different substituents on the receptor compounds. The nitro substituent - an electron withdrawing one- showed a positive effect on the binding sensitivity towards F^- and $H_2PO_4^-$ due to the strong hydrogen bonding between the receptor and the guest, while the electon-donating amino group substituent decreased the sensitivity of the sensor. Further studies will be needed to explore the effect of the substituent on the recognition behaviors.