

Preliminary communication

Synthesis and optical properties of a new class of organometallic compounds: organometallic merocyanines¹

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Abstract

A new class of organometallic compounds, organometallic merocyanines based upon the $[(\eta\text{-C}_5\text{H}_5)_2\text{Fe}_2(\text{CO})_2(\mu\text{-CO})]$ fragment acting as a donor, have been synthesized and characterized. The non-linear optical properties of these organometallic merocyanines have been determined by electric field induced second harmonic generation and indicate that these compounds have large second-order optical non-linearities.

Keywords: Organometallic; Merocyanines; Non-linear optics (NLO)

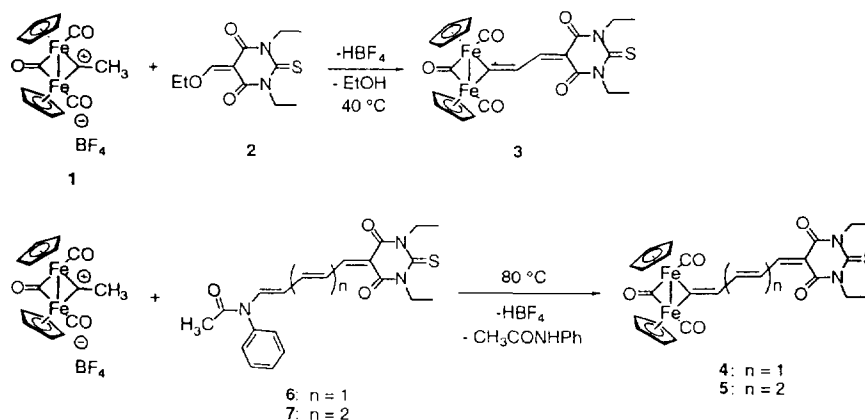
Recently, there has been intensive interest in the non-linear optical (NLO) materials due to their potential applications in photonic devices [1]. Significant advances in the underlying understanding of the structure–property relationships of these organic molecules have been made [2,3], which has resulted in the synthesis of molecules with large non-linear responses [4]. In most cases, the chromophores that exhibit large first hyperpolarizability β are π -conjugated organic molecules with donor and acceptor moieties [4]. In contrast, organometallic compounds are comparatively less explored and understood [5]. The most extensively studied system is that of the ferrocene derivatives [5,6]. However, the donor orbitals on the Fe center, for these substituted ferrocene complexes, lie at the plane of the conjugated π -system; we have hypothesized that this leads to diminished orbital overlap with the π -system and, consequently, results in a relatively poor NLO response, given the relatively low ionization potential of the ferrocene donor. We have recently suggested, therefore, that the metal should be incorporated in the same plane as the π -system in order to maximize the second-

order non-linear response [6], a concept which has been used by others as the guidance in designing new NLO materials [7]. In this paper, we would like to report the synthesis of a new class of organometallic merocyanine dyes with large second-order optical non-linearities.

As shown in Scheme 1, the di-iron ethylidene complex $[(\eta\text{-C}_5\text{H}_5)_2\text{Fe}_2(\text{CO})_2(\mu\text{-CO})(\mu\text{-CCH}_3)]^+[\text{BF}_4]^-$ (**1**) [8] can react with ethoxymethylidene-1,3-diethylthiobarbituric acid **2** through the displacement of ethoxy anion to give a neutral orange di-iron complex **3** in 87% yield. All the resonances in compound **3** are inequivalent, for example two Cp signals are observed at 5.09 and 5.03 ppm indicating the presence of restricted rotation for the di-iron cluster along the double bond between the bridging carbene carbon and the α carbon. This further suggests that the ground-state structure of **3** is best described by a limiting resonance structure of the form as shown in the depiction of the structure in Scheme 1, as opposed to a charge separated form in which there would be a low rotational barrier between what would be the bridging carbene carbon and the α carbon. The synthesis of longer chain organometallic merocyanine dyes (**4**: $n = 1$ and **5**: $n = 2$) can be accomplished through the reaction of **1** with compounds **6** and **7**. In these reactions, *N*-phenylacetamido functions as a convenient leaving group. However, the yields of the reactions are lower than those reactions

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¹ Dedicated to a friend and teacher, Professor Malcolm L.H. Green, on the occasion of his 60th birthday.



Scheme 1. Synthesis of organometallic merocyanines.

with ethoxy as the leaving group. The compounds were purified by column chromatography. Similar to **3**, NMR data, such as the coupling constants ($J_{\text{H-H}}$ values) suggest that compounds **4** and **5** adopt a somewhat bond alternated geometry in the ground state, as depicted in Scheme 1.

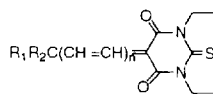
The predominantly neutral resonance form that appears to best describe the ground state for these types of molecule suggests that the di-iron fragment is not an extremely potent donor, relative to extremely strong donors that gain aromatic stabilization energy in the charge-separated form. This may be attributed partially to the substitution of the di-iron fragment with three strong π -accepting CO ligands. The compounds were characterized by ^1H and ^{13}C NMR spectroscopy, UV–vis spectroscopy, and elemental analysis. The structures were further confirmed by high resolution mass spectroscopy. Complete synthetic details and characterizing data are available as supplementary material.

The optical properties of these merocyanine dyes were studied by UV–vis spectroscopy and electrical field induced second harmonic generation (EFISH) measurements [9]. Table 1 shows a summary of the

optical data for both organometallic and organic merocyanines with a trimethylindoline donor. The relatively large $\mu\beta$ (a dot product of the dipole moment and the first hyperpolarizability) and $\mu\beta(0)$ values (corrected for dispersion using a two-level model [11]) for the organometallic merocyanines strongly indicate that the di-iron cluster is an effective donor relative to commonly used organic donors such as dimethylaminophenyl. Furthermore, the large oscillator strength of the charge transfer band in these organometallic merocyanines suggests that the metal is strongly coupled to the conjugated π -system through the mixing of metal d-orbitals with the frontier orbital of the carbon skeleton. These organometallic merocyanines are expected to possess smaller overall dipole moments than the corresponding trimethylindoline analogs due to the bridging CO ligand contributing a component to the total dipole moments that is opposite in sign to the charge transfer component. Thus, although we do not have independent measurements of μ at this time, using the reasoning alluded to above, and based on the values of the $\mu\beta(0)$ observed for the di-iron donor compared with the trimethylindoline donor (see Table 1), we

Table 1

Summary of optical data for organic and organometallic merocyanines of the form:



Compound/end groups	n	λ_{max} (nm)	ϵ ($\text{cm}^{-1} \text{M}^{-1}$)	f^a	$\mu\beta (\times 10^{48})$ (esu)	$\mu\beta(0) (\times 10^{48})$ (esu)
$\text{R}_1\text{R}_2 = (\eta\text{-C}_5\text{H}_5)_2\text{Fe}_2(\text{CO})_2(\mu\text{-CO})$	1	474	51000	0.69	170	120
$\text{R}_1\text{R}_2 = (\eta\text{-C}_5\text{H}_5)_2\text{Fe}_2(\text{CO})_2(\mu\text{-CO})$	2	564	71000	0.84	1100	660
$\text{R}_1\text{R}_2 = (\eta\text{-C}_5\text{H}_5)_2\text{Fe}_2(\text{CO})_2(\mu\text{-CO})$	3	646	55000	0.94	3100	1500
$\text{R}_1\text{R}_2 = $	1	494	126000		–340	–229
	2	592	200000		462	249
	3	686	200000		2730	1092

^a f is the oscillator strength of the transition, defined as $4.32 \times 10^{-9} \int_{\nu_1}^{\nu_2} \epsilon d\nu$, where ϵ is the extinction coefficient, ν (cm^{-1}) is the frequency, and ν_1 and ν_2 correspond to the frequencies for the edges of the band [10].

^b Ref. [3].

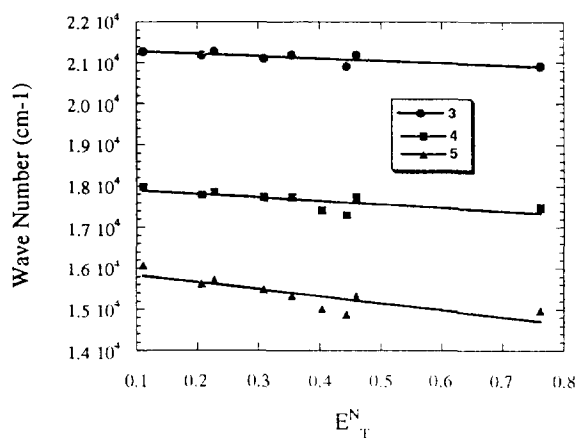


Fig. 1. Plot illustrating positive solvatochromic behavior of 3–5.

speculate that $\beta(0)$ for the organometallic merocyanines is in fact significantly greater than that for organic analogs with the trimethylindoline donor. Attempts to increase the donor strength of the di-iron system by substitution of CO for other electron-rich ligands, such as phosphine, resulted in decomposition products from which the desired chromophores could not be isolated by chromatography.

In order to understand the solvatochromic behavior of these organometallic merocyanines, the transition energies of these compounds were determined in several solvents of different polarities. Fig. 1 shows a plot of the transition energy (in wavenumbers) vs. the normalized E_T^N scale [10]. These compounds exhibit positive solvatochromic behavior (i.e. as the polarity of the solvents increases, the λ_{\max} moves to the longer wavelength). This indicates that the first excited state is more polar than the ground state, consistent with the observed positive non-linearity, within the context of the two-level model [11].

In summary, we have developed a new general synthetic strategy to a class of organometallic merocyanine dyes. These compounds possess interesting optical properties and large second-order non-linearities. We have demonstrated that the incorporation of a transition metal into the plane of π -conjugated system gives rise to improved coupling between the metal center and the organic fragment, resulting in a nearly optimal molecular non-linearity. We are currently developing the syntheses of other types of organometallic chromophore using similar design strategies.

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