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Ferrocene based D- π -A dyes as novel photoredox catalysts in photopolymeization under soft visible LED irradiations

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1	Synthesis and electrochemical, linear and third-order nonlinear optical
2	properties of ferrocene-based D- π -A dyes as novel photoredox catalysts in
3	photopolymerization under visible LED irradiations
4	
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15	
16	Abstract
17	
18	Four ferrocene-based D- π -A dyes with effective intramolecular charge transfer (ICT) properties
19	are designed and synthesized. These dyes can be used as new photoredox catalysts in free radical
20	photopolymerization under soft blue and green LED irradiations. Different π -conjugation bridge

- 21 molecules contained in the molecular structures have been shown to affect the photoreactivities of
- 22 the synthesized dyes in the photoinitiating systems. The UV-Vis absorption, electrochemical, and

23	third-order nonlinear optical properties are investigated. Experimental results are completed with
24	theoretical calculations to gain further insight into the ICT of the dyes with different π -conjugation
25	bridge molecules. A good correlation of the π -conjugation bridge molecule changes of the dyes
26	with the experimental results is established.
27	
28	Keywords
29	
30	ferrocene derivatives; organometallic dye; photoredox catalyst; third-order nonlinear optical
31	
32	1. Introduction
33	
34	Organometallic dyes with intramolecular charge transfer (ICT) properties have been already
35	successfully applied in polymerization reactions as photocatalysts due to their intense visible light
36	absorption, relatively long excited states, and suitable redox potential [1-10]. The photocatalysts
37	regenerate during the initiation step through either an oxidative cycle or a reductive cycle with
38	other additives (Scheme. 1). In an oxidative cycle, the photocatalyst is generally oxidized by an
39	electron acceptor (e.g. iodonium salt) under light irradiation, first and then recovered through the
40	reduction of an electron donor (e.g. amine). During the process, inactive radical is consumed and
41	new active radical is produced thereby considerably increasing polymerization efficiency [11-13].



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Scheme 1 Reductive and oxidative photoredox catalytic cycles

The search of photocatalysts based on low-cost metals, such as complexes based on zinc, 44 copper, and iron metals is interesting in free radical and cationic photopolymerization under 45 46 visible LED irradiations. Ferrocene (Fc) and its derivatives are important parts because of their 47 unique electrochemical and optical properties [14]. Recently, Jacques Lalevée et al. reported that a series of zinc- [15], copper- [16, 17], and iron- [18-20] based complexes have been developed as 48 49 photocatalysts in photopolymerization. Excellent photoinitiation efficiency can be achieved using 50 very low concentrations of metal-based complexes as photocatalysts in the systems due to the 51 photocatalytic effect [21].

52 Fc-based D- π -A dyes as photoredox catalysts are still seldom used in photopolymerization 53 under visible LED irradiations. We synthesized some Fc derivatives (FcIns) (Fig.1) to exploit 54 novel organometallic photocatalyst and investigate the influence of π -conjugation bridge 55 molecules with different natures on light absorption, electrochemistry, and third-order nonlinear optical properties of Fc based D- π -A dyes. In these derivatives, Fc as electron donor was attached 56 57 to indan-1,3-dione as electron acceptor through benzene, thiophene, carbazole, and phenothiazine moieties as π -conjugation bridge. The UV-Visible absorption properties and redox potentials were 58 59 investigated, and a good correlation between the experimental and theoretical (computed by 60 employing DFT and TD-DFT) results was achieved. Their nonlinear absorption coefficient β and

61 two photo absorption cross section σ were obtained using Z-scan method. Moreover, 62 photopolymerization experiments were carried out to evaluate the photoredox catalysis ability of 63 the **FcIns** under visible LED irradiations. The photocatalysis mechanism was proposed and 64 discussed.



74 procedures presented in detail in the Supporting Information. The FcCHOs were synthesized *via*

- 75 Sonogashira coupling of ethynylferrocene with 1, 2, 3, and 4 in the presence of Pd catalyst,
- triphenylphosphine and triethylamine as the base in DMF as the solvent. The **FcIns** were obtained

via Knoevenagel condensation of **FcCHOs** with indan-1,3-dione in the presence of piperidine as

78 the base in methanol/toluene (1:1, v/v) as the solvent.

The **FcIns** were characterized using spectral techniques including NMR (¹H, and ¹³C), IR, and HRMS. These characterization data fully support the obtained structures. The ¹H NMR and ¹³C NMR spectra are present in Fig. S1-S22. In the ¹H NMR spectra of the **FcIns**, the peaks at $\delta =$ 4.1–4.7 ppm are attributable to the **Fc** moiety (9 H). The peaks at $\delta = 0.7$ –4.5 ppm are attributable to the alkyl group. The high field chemical shift ($\delta = 6.7$ –9.7 ppm) stems from double bonds, benzene, thiophene carbazole, and phenothiazine moieties.



91 temperature and presented in Fig. 2. Their maximum absorption wavelengths are gathered in Table

92 S1. As shown in Fig. 2, the absorption spectra exhibit an intense band in the region of 350–500 nm

and 400–600 nm for FcIn1-3 and FcIn4, respectively, which are attributed to $\pi \to \pi^*$ transitions [22, 23]. The bands below 350 nm are attributed to the absorption of bridges and Fc moiety [24]. The $\pi \to \pi^*$ transitions exhibit red-shifted absorption as the extent of electron conjugation and electron density of bridge molecules increase. In addition, the absorption spectra of FcIn1 and FcIn2 exhibit a distinct bands around 500–600 nm mainly arise from ICT transitions [25]. However, the band is not observed for FcIn3 and FcIn4. This may be due to the overlap of charge transfer absorption with the $\pi \to \pi^*$ absorption [26]. The charge transfer in FcIn1 and FcIn2 is





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Fig. 2 UV-Vis spectra of the **FcIns** in DCM ($c = 1 \times 10^{-5}$ M).

104 TD-DFT calculations were carried out to determine the effect of varying the bridge molecules 105 on optical properties comprehensively and create a tentative assignment of the electronic 106 transitions involved in the experimental absorption spectra. The calculated electronic absorption 107 data show good correlation with the experimental data. And the assignments of the relevant 108 transitions to the absorption bands are shown in Table S1. The optimized geometries as well as the 109 frontier orbitals (HOMO and LUMO) are shown in Fig. 3 and the data are gathered in Table 2. The

110	electron density is mainly located on the Fc, alkyne, and bridge molecules of HOMO. By contrast,
111	in the LUMO, the electron density is mainly located on the indanone unit and bridge molecules for
112	the FcIns . Other representative frontier molecular orbitals of the FcIns are shown in Fig. S23.
113	As shown in Table S1 and Fig. S23, the lower energy band (509 nm) of FcIn1 originating
114	from HOMO-1 to LUMO+5, HOMO to LUMO are assigned as Fe to Cp ring transitions (MLCT)
115	with comparable contributions from $\pi \to \pi^*$ and D \to A transitions [27, 28]. The highest intensity
116	band (429 nm) of FcIn1 mainly originating from HOMO-2 to LUMO is assigned as $\pi \to \pi^*$
117	transitions. The same situation is found for FcIn2. However, for FcIn3 and FcIn4, the lowest
118	energy band (463 nm for FcIn3, 528 nm for FcIn4) mainly originating from HOMO-LUMO is
119	assigned as $\pi \to \pi^*$ transitions and $D \to A$ transitions as electron density is shifted from the donor
120	(Fc and bridge molecules) toward the acceptor (indanone). Moreover the high energy bands (250–
121	400 nm) can be assigned as $\pi \to \pi^*$ transitions of carbazole and phenothiazine moieties and d-d
122	transitions of Fc [29, 30].
123	



125 Fig. 3 Illustration of optimized geometries and frontier molecular orbitals of the FcIns at

126 B3LYP/6-31G (d, p) level of theory.

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128 **2.3 Electrochemical studies**

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130 The electrochemical properties of the **FcIns** were recorded in DCM containing 131 tetrabutylammonium hexafluorophosphate as the supporting electrolyte using cyclic voltammetry 132 (CV) methods at a scan rate of 50 mV• s⁻¹. $E_{1/2}$ values are taken as the half-wave point between 133 the forward and reverse peak for each reversible redox process. The partial CV curves of the 134 **FcIns** mainly about the **Fc** unit are shown in Fig.4 and the corresponding data are shown in Table 135 1. The full CV curves of the **FcIns** are presented in Fig. S24.





Fig. 4 Cyclic voltammograms of the **FcIns** in DCM (vs. Ag/Ag⁺)

Table 1 Electrochemical data of **Fc** and the **FcIns** obtained from **Fig.4** in DCM.

	$E_{\mathrm{pa}}^{a}\left(\mathrm{V}\right)$	$E_{\rm pc}^{\ a}({\rm V})$	$E_{1/2}^{b}(V)$	$i_{\rm pa}\left({\rm A} ight)$	$i_{\rm pc}$ (A)
Fc	0.161	0.085	0.123	2.061×10^{-5}	-1.574×10^{-5}
FcIn1	0.357	0.289	0.323	$1.320\times10^{\text{-5}}$	$-8.898 imes 10^{-6}$
FcIn2	0.371	0.299	0.335	1.345×10^{-5}	$-8.680 imes 10^{-6}$
FcIn3	0.292	0.224	0.258	$1.301\times10^{\text{-5}}$	-8.531×10^{-6}
FcIn4	0.297	0.229	0.263	$9.590\times10^{\text{-}6}$	-8.349×10^{-6}
	0.652	0.581	0.616	1.410×10^{-5}	-3.320×10^{-6}

141 ^{*a*} E_{pa} and E_{pc} correspond to the cathodic and anodic peak potentials (vs. Ag/Ag⁺), respectively. ^{*b*}

142 Half-wave potential, $E_{1/2} = (E_{pa} + E_{pc})/2$.



moiety and acceptor moieties. The presence of acceptor moieties result in the lower electron

150	density at the Fc moiety and inhibition of oxidation of Fc [28].
151	FcIn1 and FcIn2 show nearly identical $E_{1/2}$ values ($\Delta E_{1/2} = 0.012$ V FcIn1 \rightarrow FcIn2). This
152	result can be attributed to the slight difference in the energies of HOMO of FcIn1 and FcIn2
153	(Table 2). The same situation is also found between FcIn3 and FcIn4 ($\Delta E_{1/2} = 0.005$ V FcIn3 \rightarrow
154	FcIn4). However, by increasing the extent of electron conjugation and electron density of bridge
155	molecules, a relatively large cathodic shift in $E_{1/2}$ values is observed (e.g. $\Delta E_{1/2} = 0.065$ V FcIn1
156	\rightarrow FcIn3; $\Delta E_{1/2} = 0.060$ V FcIn1 \rightarrow FcIn4, Table 1). This result reflects a decreased electronic
157	communication between donor and acceptor moieties of FcIn3 and FcIn4. This observation is in
158	accordance with increased energy of the HOMO in FcIn3 and FcIn4 compared with that in FcIn1
159	and FcIn2 (Table 2) [32-34].
160	The onset potentials for the oxidation E_{ox}^{onset} and reduction E_{red}^{onset} were determined from the CV
161	curves according to the literature methods [35] (Fig. S25-28, Table S2). The experimental and
162	theoretical HOMO and LUMO energy levels are summarized in Table 2. As shown in Table 2, the
163	energy values of HOMO and LUOM obtained from CV data ($E_{HOMO/CV}$, $E_{LUMO/CV}$) and theoretical
164	calculations (E_{HOMO} , E_{LUMO}) exhibit essentially the same trend. The electrochemical band gaps

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170 **Table 2**

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 $E_{\rm g/CV}$ obtained from electrochemical measurements are smaller than optical band gap $E_{\rm g/opt}$

obtained from UV-Vis absorption spectra. The solvent-solute interaction and interactions between

the analyte and the electrode surface may responsible for this discrepancy [36, 37]. Moreover, this

discrepancy results in the different values of $E_{LUMO/CV}$ and $E_{LUMO/opts}$.

- 171 Comparison of the experimental (CV/UV-Vis absorption spectra) and calculated (TD-DFT)
- 172 HOMO-LUMO and band gaps of the **FcIns**.
- 173

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	Experimental data					T	TD-DFT calculations ^a			
	$E_{\text{HOMO/CV}}^{b} E_{\text{LUMO/CV}}^{b}$		$E_{\rm g/CV}^{b}$	$E_{ m g/opt}^{\ \ c} E_{ m LUMO/opt}^{\ \ d}$		E	номо	E _{LUMO}	ΔΕ	
	(eV)	(eV)	(eV)	(eV)	(eV)	((eV)	(eV)	(eV)	
FcIn1	-4.925	-3.629	1.296	2.127	-2.798	-5	.491	-2.612	2.879	
FcIn2	-4.944	-3.641	1.303	1.984	-2.960	-5	.495	-2.688	2.807	
FcIn3	-4.862	-3.346	1.516	2.375	-2.487	-5	.120	-2.286	2.834	
FcIn4	-4.864	-3.409	1.455	1.959	-2.905	-5	.045	-2.423	2.622	

175 ^{*a*} Calculating on the TD-DFT/B3LYP/ Genecp (SDD/6-31G (d, p)) level. ^{*b*} Calculated as $E_{\text{HOMO/CV}}$ 176 $= -e[E_{\text{ox}}^{\text{onset}} - E_{1/2(\text{Fc/Fc+})} + 4.8], E_{\text{LUMO/CV}} = -e[E_{\text{red}}^{\text{onset}} - E_{1/2(\text{Fc/Fc+})} + 4.8], E_{g/\text{CV}} = E_{\text{LUMO/CV}} - E_{\text{HOMO/CV}}$ 177 $(E_{\text{ox}}^{\text{onset}} \text{ and } E_{\text{red}}^{\text{onset}} \text{ were obtained from Table S2}).$ ^{*c*} $E_{g/\text{opt}}$ estimated from the UV–Vis absorption 178 spectra. ^{*d*} Calculated as $E_{\text{LUMO/opt}} = E_{g/\text{opt}} + E_{\text{HOMO/CV}}$. 179

180 2.4 Third-order nonlinear optical properties

181

Since the FcIns all exhibit one-photo absorption at 500–600 nm, they may exhibit 2PA at 1000– 1200 nm. The nonlinear absorption of the FcIns was measured with picosecond laser excited at 1206 nm, where the dyes show no linear absorption. The typical open–aperture Z-scan traces of the FcIns are shown in Fig. 5. The squares represent the experimental data, and the solid curve is the fitting line.

187 As can be seen, the open-aperture traces exhibit a clear dip, all the dyes in tetrahydrofuran 188 (THF) solution exhibits a reverse saturated absorption optical property. The corresponding 189 nonlinear absorption coefficients β and 2PA cross sections σ were calculated. Table. 3 lists the

190 results.

191 FcIn1 and FcIn2 exhibit higher 2PA cross section than FcIn3 and FcIn4. All the dyes have 192 the same donor and acceptor parts. Thus, the bridge molecules may play a key role in the third-order nonlinear properties of the FcIns. The order of the σ values for the dyes is FcIn1 \approx 193 194 FcIn2 > FcIn4 > FcIn3, although, FcIn4 and FcIn3 have relatively large planar structure in the molecular level. It is known that NLO properties are directly related to the ICT character of 195 molecules [38-40]. The relatively efficient charge transfer of FcIn1 and FcIn2 can account for the 196 197 observed trend of the σ values. This result is in accordance with that observed from the UV-Vis 198 absorption and electrochemistry study. In addition, FcIn3 exhibits the smallest 2PA cross section, besides the ICT factor, the weakest one-photo absorption at 500-600 nm may also responsible for 199 200 the result. For comparison, Rhodamine B (RB), a commonly used 2PA dye, and Fc were tested 201 under the same experimental conditions using Z-scan method. The results are listed in Table 3 and Fig. S29. 202



Fig. 5 Normalized open-aperture Z-scan transmittance of the **FcIns** in THF in a 1 mm cell at 1064

205 nm with a fitting curve (red lines).

	FcIn1	FcIn2	FcIn3	FcIn4	RB
nonlinear absorption coefficient β (cm/GW)	3.76	3.67	1.29	2.91	1.16
2PA cross section σ (10 ⁴ GM)	5.83	5.69	2.00	4.51	1.80
2.5 Free radical photo2.5.1 Photoinitiating Ab	polymerizatio	n (FRP) Ins based photo	initiating syster	ns for FRP	
			5		
All the dyes exhibit re	latively high a	absorption in th	e region of vis	ible light, whic	h make them
possible photoredox ca	talysts to initia	ate free radical	polymerization	under long-wa	velength light
sources. The FRP of tr	ipropylene gly	col diacrylate (TPGDA) in the	e presence of tw	vo-component
photoinitiating systems	were carried	out under blue	LED according	g to the photop	olymerization
experiments (see exper	imental details	s). The double	bond conversio	n rate vs. time	curves of the
photocurable resin film	s containing d	ifferent FcIns v	vere obtained, a	and the results v	vere shown in
Fig. 6. When using th	ne FcIns or (ONI alone in T	PGDA, no eff	fective polymer	izations were
observed under blue LE	D irradiation ((Fig. S30).			
As shown in Fig. 6	(a), the FRP	of the FcIns /O	NI is efficient	in terms of fina	l conversions
(FCs) under blue LED	. The conversi	ions can reach	to 8%, 7%, 45	%, and 82% fo	r FcIn1 /ONI,
FcIn2/ONI, FcIn3/ON	I, and FcIn4/0	ONI, respectivel	y, when the irr	adiation time w	vas 100s. And
the FCs was approxin	nately 56%, 7	74%, 86%, and	87%, respect	ively, for the	corresponding

206	Table 3 Third-order nonlinear optical parameters for the FcIns and RB at 1064 nm.
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two-component photoinitiating systems. It is clear that the order of FRP efficiencies under blue
LED is FcIn4/ONI > FcIn3/ONI > FcIn2/ONI > FcIn1/ONI. The relatively high initiating
efficiency of FcIn4/ONI and FcIn3/ONI may be due to the good photosensitization ability of
phenothiazine and carbazole moieties contained in FcIn4 and FcIn3 in photoinitiating systems
[41-43]. Under green LED, only FcIn4/ONI has the initiating ability for FRP (Fig. 6 (c), FCs =
76%), which can be caused by the relatively low absorption under green LED for other FcIns (see
Fig. 2).

231 photoinitiating (FcIns/ONI/NMP) photopolymerization Three-component systems 232 experiments were also studies. Interestingly, the results are quite different from those of two-component photoinitiating systems. The initiating efficiency is increased markedly, especially 233 for FcIn1 and FcIn2. As shown in Fig. 6 (b), the conversion can reach up to 52% and 90% for 234 235 FcIn1/ONI/NMP and FcIn2/ONI/NMP (only 8% and 7% for their corresponding two-component systems), when the irradiation time was 100s. The FCs was approximately 93%, 92%, 92%, and 236 90%, for FcIn1/ONI/NMP, FcIn2/ONI/NMP, FcIn3/ONI/NMP, and FcIn4/ONI/NMP, 237 238 respectively, which all higher than their corresponding two-component photoinitiating systems. 239 The order of FRP efficiencies under blue LED is FcIn2/ONI/NMP > FcIn3/ONI/NMP > 240 FcIn4/ONI/NMP > FcIn1/ONI/NMP. Under green LED, FcIn2/ONI/NMP also exhibit good initiating efficiency for FRP besides FcIn4/ONI/NMP (Fig. 6 (c)). No polymerization was 241 242 observed when using NMP alone in photopolymerization experiments (Fig. S30). Recently, the 243 intermolecular charge transfer complexes between amine and iodonium are proposed as highly 244 efficient photoinitiating systems [44], however, the charge transfer complex was not observed for ONI/NMP in DCM (Fig. S31) and no polymerization was observed using ONI/NMP in 245





266 of the **FcIns**, and the electrostatic interaction energy of the initially-formed ion pair, which is 267 generally considered to be negligible in polar solvents. The results are gathered in Table. 4. The 268 calculated $\Delta G_{\rm S}$ values were all negative, which confirms that the process was thermodynamically 269 favoured [45, 46].



271 Fig. 7 Steady state photolysis of (a) FcIn1 alone and (b) FcIn1/ONI in THF upon the blue LED

exposure ([FcIn1] = 7.54×10^{-5} M, [ONI] = 1.47×10^{-3} M); UV-Vis spectra recorded at different

273 irradiation times (m = minute).

274

270

275 Table 4

- 276 Light absorption molar extinction coefficients (ε) of the **FcIns** at the emission wavelengths of the
- 277 LEDs and the parameters characterizing the photochemistry reactivity of the FcIns with ONI.

2	7	o
2	1	o

	ϵ_{460nm} (M ⁻¹ cm ⁻¹)	ϵ_{520nm} (M ⁻¹ cm ⁻¹)	$E_{\rm ox}^{\ a}$ (V/SCE)	$E_{\rm red}^{\ a}$ (V/SCE)	$E_{\rm S}^{\ c}$ (eV)	$\Delta G_{\rm S}^{\ d}$ (eV)
FcIn1	7600	6900	0.617	-0.938	2.014	-0.717
FcIn2	29625	9800	0.631	-0.899	1.982	-0.671
FcIn3	36100	4100	0.552	-1.148	2.095	-0.863
FcIn4	11200	26600	0.557	-1.072	2.085	-0.848
ONI	0	0		-0.68^{b}		

279

280 ^{*a*} E_{ox} and E_{red} were obtained from Table S2 ($E_{1/2 \text{ (Fc/Fc+)}} = 0.38 \text{ V}$ vs. SCE [47], $E_{1/2 \text{ (Fc/Fc+)}} = 0.123 \text{ V}$

281 vs. Ag/Ag⁺). ${}^{b}E_{red}$ (ONI) = -0.68V [48]. c Calculated on the TD-DFT/B3LYP/Genecp (SDD/6-31G

282 (d, p)) level. ^d Calculated from the classical Rehm–Weller equation.



293

***FcIns** (II) + Ar₂I⁺ \rightarrow **FcIns** (III) + Ar₂I[•] \rightarrow ArI + Ar[•] (r2)



294

Fig. 8 Photolysis kinetics of FcIns/ONI and FcIns/ONI/NMP measured under blue LED ([FcIn1] = 7.54×10^{-5} M, [FcIn2] = 7.44×10^{-5} M, [FcIn3] = 5.96×10^{-5} M, [FcIn4] = 5.64×10^{-5} M,

297 [ONI] =
$$1.47 \times 10^{-5}$$
 M, and [NMP] = 1.35×10^{-2} M).

298

Remarkably, when incorporating NMP in three-component **FcIns**/ONI/NMP systems, additional reactions that convert Ar' into very reactive NMP' (-H) radical *via* H-abstraction reactions (r3) and regenerate **FcIns** through reduction of **FcIns** (III) by NMP will take place (r4, r5) [17]. The photolysis efficiencies of the **FcIns**/ONI and **FcIns**/ONI/NMP in THF were calculated from the A/A_0 ratio, where A is the absorbance of the assigned wavelength (**FcIn1**: 385nm, **FcIn2**: 426nm, **FcIn3**: 447nm, and **FcIn4**: 309nm) at different irradiation times and A_0 is the absorbance before irradiation. These data are presented in Fig. 8.

As shown in Fig. 8 (a), the photolysis of **FcIn1** in the three-component systems (**FcIn1**/ONI/NMP) is much slow than in the two-component systems (**FcIn1**/ONI). The same situation is also found in **FcIn2** based systems (Fig. 8 (b)). The redox potential of NMP was

309	measured using CV methods (Fig. S32). As shown in Fig. S32, three oxidation signals are
310	observed ($E_{ox1} = -0.031V$, $E_{ox2} = 0.501V$, and $E_{ox3} = 0.897V$ vs. Ag/Ag ⁺). The reduction potential
311	of FcIns (III) (e.g., 0.357V vs. Ag/Ag ⁺ for FcIn1 in Table S2) is higher than E_{ox1} and close to E_{ox2}
312	of NMP. These results can support reaction 4 (r4) and highlight a regeneration of these two FcIns
313	in the presence of NMP [12, 50]. The regeneration of these two FcIns ensures a photoredox
314	catalyst behavior in line with an improved reactivity. This is in full agreement with the
315	photopolymerization experimental results which show that the performance of the
316	three-component systems is much better than that of two-component systems for FcIn1 and FcIn2
317	(see Fig. 6) [51]. However, for FcIn3, the photolysis rate of the three-component system is faster
318	than that of the two-component system (Fig. 8 (c)). This may be due to that NMP mainly occur
319	reaction 3 (r3) in FcIn3 based photoinitiating system. Newly formed reactive radical NMP [•] (-H
320	show improved efficiency in FcIn3/ONI/NMP from the photopolymerization experimental results
321	The photolysis rate of FcIn4 is nearly the same in two-component and three-component systems
322	(Fig. 8 (d)). The result is in accordance with the performance of FcIn4 based photoinitiating
323	systems in photopolymerization experiments.
324	$Ar^{\bullet} + NMP \rightarrow Ar - H + NMP^{\bullet}_{(-H)}$ (r3)
325	$\mathbf{FcIns} (III) + \mathbf{NMP} \rightarrow \mathbf{FcIns} (II) + \mathbf{NMP}^{+} $ (r4)
326	$NMP^{\bullet+} \rightarrow NMP^{\bullet}_{(-H)} + H^{+} $ (r5)
327	
328	
329	3. Conclusion

Four Fc-based D- π -A dyes with different bridge molecules were designed and synthesized 331 332 successfully. As deduced from the UV-Vis absorption spectra and quantum chemical calculations, 333 all the dyes exhibited evident ICT character. The $\pi \to \pi^*$ transitions red shifted as the electron density and conjugation extent of bridge molecules increased. These results combined with 334 electrochemistry results indicated that **FcIn1** and **FcIn2** with relatively short π -conjugation bridge 335 length had more efficient charge transfer than FcIn3 and FcIn4. All the FcIns showed nonlinear 336 absorption at 1064 nm, and the nonlinear absorption properties were influenced by the ICT 337 character and the one-photo absorption ability at 500-600 nm. In addition, the FcIns/ONI 338 339 photoinitiating systems could initiate FRP of TPGDA under blue and green LED irradiations. With the addition of NMP, the initiation efficiency of the three-component (FcIns/ONI/NMP) 340 photoinitiating systems was remarkably increased due to the photocatalytic effect of the FcIns. 341 342 The photocatalytic mechanisms were proposed and studied by steady state photolysis and cyclic voltammetry. Efficient photoredox catalysts that feature abundant, low-cost, and low-toxic Fc 343 derivatives are being developed continuously. The present study is expected to facilitate the design 344 345 and potential application of Fc derivatives.

346

347 4. Experimental details

- 348
- 349 4.1 Materials and instruments
- 350

All the reactants and solvents used in this work are commercial available and without further
purification. Indan-1,3-dione, 4-bromobenzaldehyde, 5-bromothiophene-2-carbaldehyde, and
N-methylpyrrolidone (NMP) were purchased from Beijing Chemical Works (Beijing, China).

354	Ethynylferrocene, 6-bromo-9-ethyl-9 <i>H</i> -carbazole-3-carbaldehyde, and
355	7-bromo-10-ethyl-10 <i>H</i> -phenothiazine-3-carbaldehyde were synthesized according to the reference
356	method [52-54]. The catalyst $Pd(PPh_3)_2Cl_2$ and iodonium bis (4-methylphenyl)
357	hexafluorophosphate (ONI) was also prepared according to the reference method [55].
358	Tripropylene glycol diacrylate (TPGDA, from Guangzhou Lihou Trading Co. Ltd, China) was
359	chosen as the monomer for free radical photopolymerization.
360	¹ H NMR (400 MHz) and ¹³ C NMR (101 MHz) spectra were recorded on an NMR
361	spectrometer (Bruker AV400). FT-IR (KBr) spectra were recorded on a Nicolet 5700 instrument
362	(Thermo Electron Corporation, Waltham, MA). Mass spectra were measured with an LC/MSD
363	mass spectrometer. Melting points were measured with an XT-4 microscopic melting point
364	apparatus. The UV-vis spectra were obtained using a UV-5200 (UNICO) UV-Vis
365	spectrophotometer. Elemental analysis was performed on an Elementar Vavio Elcube.
366	The chip on board (COB) light sources were used for the irradiation of the photocurable
367	samples: blue LED (JH-100B14G30-Z1C, 460 nm) and green LED (JH-100G14G30-Z1C, 520
368	nm). The power of COB light sources is 30 W.

369

370 4.2 Synthesis of the FcIns

371

372 General procedure for the synthesis of the FcIns

373 A mixture of 0.31g (1mmol) FcCHO1, 0.22g (1.5mmol) indan-1,3-dione were dissolved in

toluene/methanol (6mL, 1:1, v/v), then 0.1 mL piperidine was added. The mixture was stirred for

4 at 80°C. After completion of the reaction (TLC), the mixture was cooled down to the room

376	temperature. The solid precipitate was collected and purified by silica gel with petroleum
377	ether/ethyl acetate (5:1, v/v) as eluent to afford a dark red solid FcIn1 . Yield: 75%. Following the
378	above procedure and using FcCHO2, FcCHO3, and FcCHO4 instead of FcCHO1 obtained
379	FcIn2, FcIn3, and FcIn4, respectively.
380	2-(4-(ferrocenyl-ethynyl)benzylidene)-1 <i>H</i> -indene-1,3(2 <i>H</i>)-dione (FcIn1) [30]
381	Dark red solid. Yield: 75%. Mp: 253-256 °C. ¹ H NMR (400 MHz, CDCl ₃) δ (ppm) 8.46 (d, $J = 8.2$
382	Hz, 2H), 8.05 – 7.97 (m, 1H), 7.86 (s, 1H), 7.84 – 7.77 (m, 1H), 7.59 (d, J = 8.2 Hz, 2H), 4.57 (s,
383	2H), 4.32 (s, 2H), 4.28 (s, 5H); ¹³ C NMR (101 MHz, CDCl ₃) δ (ppm) 190.28, 189.13, 145.88,
384	142.59, 140.13, 135.41, 135.23, 134.19, 132.12, 131.48, 129.17, 128.99, 123.35, 123.33, 94.05,
385	86.19, 71.86, 70.29, 69.56, 64.60. IR (KBr, $\tilde{\nu}$ (cm ⁻¹)): 3083, 3056 (Ar-H), 2197 (C=C), 1729,
386	1682 (C=O), 1618, 1585 (Ar), 1420, 1206, 1190 (Cp), 821 (Cp-H), 498 (C-Fe). HRMS (ESI): <i>m</i> / <i>z</i>
387	calculated for $C_{28}H_{18}FeO_2$ 442.0656 [M ⁺]; found 443.3324 [M + H ⁺]. Anal. Calcd. for $C_{28}H_{18}FeO_2$:
388	C 76.04, H 4.10, Fe 12.63, O 7.23; found: C 76.34, H 4.03, O 7.34.
389	2-((5-(ferrocenyl-ethynyl)thiophen-2-yl)methylene)-1 <i>H</i> -indene-1,3(2 <i>H</i>)-dione (FcIn2)
390	Dark red solid. Yield: 72%. Mp: > 350 °C. ¹ H NMR (400 MHz, CDCl ₃) δ (ppm) 7.98 (m, 2H),
391	7.92 (s, 1H), 7.84 (s, 1H), 7.79 (m, 2H), 4.58 (s, 2H), 4.36 (s, 2H), 4.30 (s, 5H); ¹³ C NMR (101
392	MHz, CDCl ₃) δ (ppm) 190.29, 189.55, 142.37, 142.29, 140.55, 137.25, 135.54, 135.15, 134.97,
393	131.81, 124.62, 123.09, 123.01, 106.05, 100.59, 79.60, 71.90, 70.43, 69.95. IR (KBr, $\tilde{\nu}$ (cm ⁻¹)):
394	3076 (Ar-H), 2197 (C=C), 1716, 1677 (C=O), 1596, 1579 (Ar), 1419, 1203, 1098 (Cp), 810
395	(Cp-H), 483 (C-Fe). HRMS (ESI): m/z calculated for C ₂₆ H ₁₆ FeO ₂ S 448.0220 [M ⁺]; found
396	449.3021 [M + H ⁺]. Anal. Calcd. for $C_{26}H_{16}FeO_2S$: C 69.66, H 3.60, Fe 12.46, O 7.14, S 7.15;
397	found: C 68.96, H 3.26, O 7.24, S 7.21.

398

399 2-((9-ethyl-6-(ferrocenyl-ethynyl)-9*H*-carbazol-3-yl)methylene)-1*H*-indene-1,3(2*H*)-dione

400 (FcIn3)

401	Red solid. Yield: 82%. Mp: 243-246 °C ¹ H NMR (400 MHz, CDCl ₃) δ (ppm) 9.63 (s, 1H), 8.55 (d
402	<i>J</i> = 8.6 Hz, 1H), 8.41 (s, 1H), 8.10 (s, 1H), 8.04 (d, <i>J</i> = 5.8 Hz, 1H), 8.00 (d, <i>J</i> = 5.6 Hz, 1H), 7.80
403	(s, 2H), 7.65 (d, J = 8.1 Hz, 1H), 7.47 (d, J = 8.6 Hz, 1H), 7.39 (d, J = 8.2 Hz, 1H), 4.59 (s, 2H),
404	4.40 (d, $J = 7.1$ Hz, 2H), 4.32 (s, 5H), 4.29 (s, 2H), 1.49 (t, $J = 6.9$ Hz, 3H); ¹³ C NMR (101 MHz,
405	CDCl ₃) δ (ppm) 191.14, 189.87, 148.59, 143.53, 142.46, 140.00, 139.90, 134.97, 134.72, 133.96,
406	130.17, 128.50, 125.87, 125.30, 124.28, 123.41, 123.39, 122.98, 122.96, 116.11, 109.12, 108.90,
407	87.07, 86.43, 71.50, 70.26, 68.97, 38.15, 13.93. IR (KBr, $\tilde{\nu}$ (cm ⁻¹)): 3080 (Ar-H), 2970
408	(CH ₃ -CH ₂), 1718, 1673 (C=O), 1575, 1553 (Ar), 1387, 1104 994 (Cp), 816 (Cp-H), 485 (C-Fe).
409	HRMS (ESI): m/z calculated for C ₃₆ H ₂₅ FeNO ₂ 559.1235 [M ⁺]; found 560.3612 [M + H ⁺]. Anal.
410	Calcd. for C ₃₆ H ₂₅ FeNO ₂ : C 77.29, H 4.50, Fe 9.98, N 2.50, O 5.72; found: C 76.49, H 4.61, N
411	2.42, O 5.68.

412 2-((10-ethyl-7-(ferrocenyl-ethynyl)-10*H*-phenothiazin-3-yl)methylene)-1*H*-indene-1,3(2*H*)-di 413 one (FcIn4)

Dark red solid. Yield: 56%. Mp: 209-212 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.36 (d, J = 1.7 Hz,
1H), 8.29 (dd, J = 8.6, 1.6 Hz, 2H), 8.02 – 7.93 (m, 2H), 7.81 – 7.74 (m, 2H), 7.69 (s, 1H), 7.24
(dd, J = 8.5, 1.6 Hz, 1H), 7.19 (d, J = 1.6 Hz, 1H), 6.89 (d, J = 8.7 Hz, 1H), 6.80 (d, J = 8.5 Hz,
1H), 4.49 (s, 2H), 4.24 (s, 7H), 3.98 (q, J = 6.9 Hz, 2H), 1.47 (t, J = 6.9 Hz, 3H); ¹³C NMR (101
MHz, CDCl₃) δ (ppm) 190.74, 189.49, 148.57, 145.35, 142.43, 141.83, 140.03, 135.65, 135.04,
134.82, 132.88, 130.63, 129.86, 127.98, 126.60, 123.08, 123.03, 123.02, 122.73, 119.22, 115.01,

420	114.29, 88.93, 84.62, 71.37, 69.99, 68.86, 65.22, 42.72, 12.74. IR (KBr, $\tilde{\nu}$ (cm ⁻¹)): 3092 (Ar-H),
421	2979 (CH ₃ -CH ₂), 2206 (C=C), 1721, 1681 (C=O), 1595, 1563 (Ar), 1396, 1154, 1087 (Cp), 818
422	(Cp-H), 483 (C-Fe). HRMS (ESI): m/z calculated for C ₃₆ H ₂₅ FeNO ₂ S 591.0955 [M ⁺]; found
423	591.3336 [M ⁺]. Anal. Calcd. for C ₃₆ H ₂₅ FeNO ₂ S: C 73.10, H 4.26, Fe 9.44, N 2.37, O 5.41, S 5.42;
424	found: C 72.38, H 4.18, N 2.29, O 5.36, S 5.00.
425	
426	4.3 Electrochemical measurements
427	
428	The electrochemical measurements were carried out in dichloromethane (DCM) using a CHI760E
429	electrochemical workstation using cyclic voltammetry (CV) methods with tetrabutylammonium
430	hexafluorophosphate (0.1 M) as a supporting electrolyte. The concentration of the FcIns were 1 \times
431	10^{-3} M. Glassy carbon, Ag/AgNO ₃ electrode and a platinum wire were used as the working,
432	reference, and auxiliary electrode, respectively. Ferrocene (Fc) was used as a reference. The glassy
433	carbon electrode was polished with alumina slurry of 0.05 μm on a polish cloth before use. The
434	platinum wire was immersed in HNO_3 solution for 30min at 80 °C to remove metal impurities
435	prior to use. All the solutions were purged with Ar gas for 10 min before measuring and an Ar gas
436	blanket was maintained over the solution during the experiments.
437	

438 4.4 Computational details

439

440 Quantum chemical calculations were carried out with the Gaussian 09 package. All the molecular441 structures of interest were first optimized in the ground state by the density functional theory

(DFT) method at a B3LYP/ Genecp (Fe with SDD basis set and C, H, N, O, and S with 6-31G (d,
p) basic set) level of theory without any symmetry restraint. The first 50 spin-allowed singlet–
singlet excitations for the dyads were calculated by using time dependent density functional theory
(TD-DFT) at a B3LYP/ Genecp (Fe with SDD basis set and C, H, N, O, and S with 6-31G (d, p)
basic set) (cpcm, solvent=dichloromethane) level of theory. The frontier molecular orbitals
properties and electronic absorption data were analyzed and visualized using GaussView 5.0

449

448

450 4.5 Z-scan measurement

software.

451

452 The third-order nonlinear optical properties of the FcIns were measured at 1064 nm in 453 tetrahydrofuran (THF) by using the open-aperture Z-scan method. The method can provide the nonlinear absorption coefficient of samples. The samples were placed in 1mm cuvettes and then 454 irradiated by plane-polarized 25ps laser pulses from a Q-switched Nd:YAG laser (PL2210A, 455 456 EKSPLA). The laser pulse energy was 6.37µJ. The laser beam was divided into two parts. One was used as the intensity reference and the other was used for transmittance measurement. The 457 458 laser beam was focused by passing through len (f = 200 mm) and the beam focal spot radius (ω_0) was about 45µm. The position of the sample cell could be varied along the laser-beam direction 459 460 (z-axis). Assuming a Gaussian bean profile, the nonlinear absorption coefficient β can be obtained by curve fitting to the observed open-aperture traces with equation (1) [56, 57]: 461

463
$$T(z) = 1 - \frac{\beta I_0 (1 - e^{-\alpha_0 l})}{2\alpha_0 (1 + (z/z_0)^2)}$$
(1)

464

465 where α_0 is the linear absorption coefficient, l is the sample length, and $z_0 = k\omega_0^2/2$ is the 466 Rayleigh length. $k = 2\pi/\lambda$ is the wave vector; λ is the laser wavelength; I_0 is the on-axis 467 irradiance at the focus (z = 0). When $\alpha_0 l \ll 1$, equation (1) can be simplified as equation (2):

(2)

468

469
$$T(z) = 1 - \frac{\beta I_0 l}{2(1 + (z/z_0)^2)}$$

470

471 The two photo absorption cross section (in units of $1\text{GM} = 1 \times 10^{-50} \text{cm}^4/\text{s}$) can be determined by 472 utilizing $\sigma = h\nu\beta/(N_A \ d \times 10^{-3})$, where $h\nu$ is the excitation energy and N_A is the Avogadro 473 constant, *d* is the concentration of the samples (2 × 10⁻³ M).

474

475 **4.6 Photopolymerization experiments**

476

The free radical photopolymerization (FRP) experiments were carried out under laminated 477 478 conditions. The two-component photoinitiating systems are based on an FcIns/ONI (0.1/2.0% w/w) for FRP. The weight percent of the photoinitiating system is calculated from the monomer 479 480 content. Tripropylene glycol diacrylate (TPGDA, from Guangzhou Lihou Trading Co. Ltd, China) 481 was chosen as the monomer for FRP. The FcIns/ONI/monomer photosensitive formulations were 482 photocured in 0.6 mm thick plastic molds with a 5 mm diameter center. The molds were clamped between two glass slides and placed under the irradiation sources. The distance between 483 484 irradiation sources and formulations is 1.5 cm. The specimens were irradiated at different time intervals by controlling the curing light. The near-infrared spectra of uncured monomer were 485

486	obtained immediately after each exposure interval by using a Fourier transform infrared
487	spectrometer (Nicolet 5700, 4000–7000 cm ⁻¹ wavelength range). With the addition of NMP, the
488	three-component photoinitiating systems are based on an FcIns/ONI/NMP ($0.1/2.0/4.0\%$ w/w) for
489	FRP. The double bond conversion profiles were calculated from the decay of the absorption
490	intensities located at 6165 cm ⁻¹ as described by Stansbury and Dickens [58]. The double bond
491	conversion was calculated using the following equation (3):
492	
493	Conversion% = $[1 - S_t / S_0] \times 100\%$ (3)
494	
495	where S_t is the area of the C=C characteristic absorbance peak and S_0 is the initial area of the C=C
496	characteristic absorbance peak.
497	
498	Acknowledge
499	
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503	Technology CHEMCLOUDCOMPUTING Platform for support with calculations.
504	
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► Four ferrocene-indanone organometallic dyes are designed and synthesized.

- All the dyes exhibit effective intramolecular charge transfer characters and show good nonlinear absorption properties at 1064 nm.
- ► A good correlation of the structure changes with experimental and theoretical results is established.
- The synthesized dyes can be used as novel photoredox catalysts in photopolymerization under soft visible LED irradiations.