

# Electronic Supporting Information (ESI) for Structurally influenced optical nonlinearities and ultrafast dynamics in $\beta$ -acroleyl- and $\beta$ -dicyanobutadienyl- appended cobalt corroles

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## Experimental section

### Nonlinear optical studies

The NLO studies were performed using single beam fs Z-scan technique *via* open aperture (OA) and closed aperture (CA) configurations in quartz cuvette in DMF solution. A fs laser beam obtained from a Ti:Sapphire amplifier laser centred at 800 nm (120 fs, 1 kHz) was utilized to perform the Z-scan measurements. The Z-scan measurements intensity was kept constant at  $I_0 = 4.1 \times 10^{14} \text{ W m}^{-2}$ . In typical third-order NLO processes, when subjected to higher laser intensities (typically in the range of  $\text{GW/cm}^2$ ), the medium exhibits a nonlinear response to the applied electric field, resulting in the variations of both the absorption and refraction of the medium as  $\alpha(I) = \alpha_0 + \beta I$ , and  $n(I) = n_0 + n_2 I$ . Here  $\alpha_0$ ,  $n_0$  are the linear absorption and refraction coefficients, respectively, and  $I$  represent the laser intensity. In a typical Z-scan technique, a laser beam is focused using a convex lens and the transmittance through the sample is recorded at each position of the focused beam at a far field position in two different configurations. In one mode of configurations, the transmitted beam is fully collected by the photodiode, called the OA Z-scan, which provides information of the nonlinear absorption (two-photon absorption coefficient, multi-photon absorption coefficient etc.) of materials. In another configuration, the transmitted beam is collected using an aperture placed before the photodiode called the CA Z-scan, which gives information of the nonlinear refraction (nonlinear refractive index,  $n_2$ ) of materials.

### Femtosecond transient absorption studies

The fs TAS of all the investigated cobalt corroles was also performed by optical pump-probe technique in DMF solution. In optical pump-probe spectroscopy, an 800 nm laser beam of 120 fs pulse width working at 1 kHz repetition rate from a Ti:Sapphire amplifier laser was divided into two parts. One part of 800 nm was fed to an optical parametric amplifier (OPA) to generate an intense pump beam of 350 nm for UV excitation. Another part of 800 nm was focused on  $\text{CaF}_2$  crystal to generate broadband supercontinuum, which acts as a probe beam. The TAS studies for all the corroles were performed with constant pump laser energy at  $0.2 \mu\text{J}$ . To record the ultrafast dynamics, the pump and probe beams are spatially and temporally overlapped at the sample surface, and the transient change in the absorbance in the probe beam has been monitored at each delay time interval between the pump and probe.

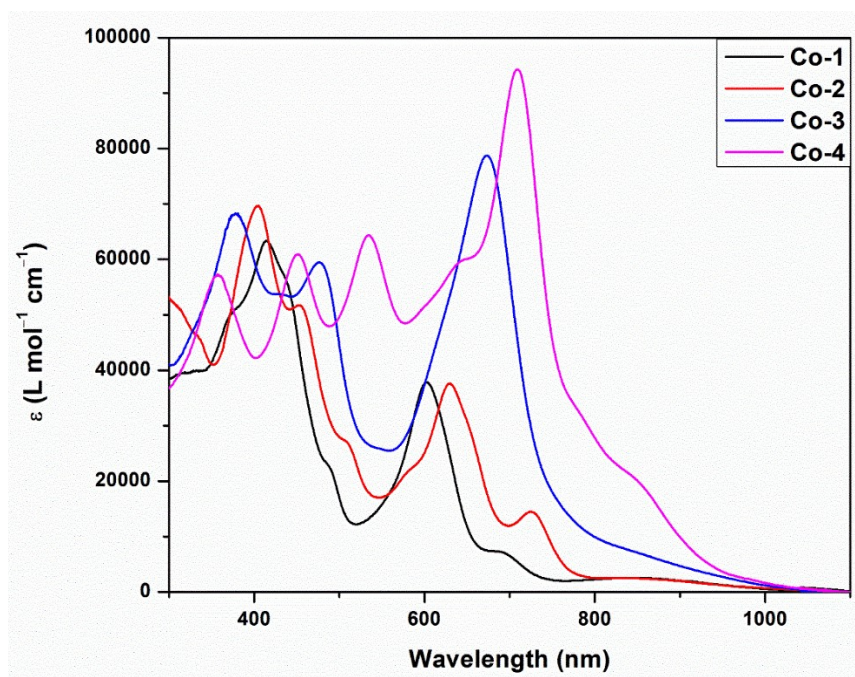
The TAS were performed by measuring the difference absorbance ( $\Delta A(\tau, \lambda)$ ) between the absorbance of pump excited sample [ $A_{exc}(\tau, \lambda)$ ] and the unexcited sample [ $A(\tau, \lambda)$ ] in the transmission geometry. The  $\Delta A(\tau, \lambda)$  has been defined as follows

$$\Delta A(\tau, \lambda) = A_{Pump-On}(\tau, \lambda) - A_{Pump-Off}(\tau, \lambda), \quad A(\tau, \lambda) = -\log \frac{(I_{\lambda}^{probe}/I_{\lambda}^{ref})_{Pump-On}}{(I_{\lambda}^{probe}/I_{\lambda}^{ref})_{Pump-Off}}$$

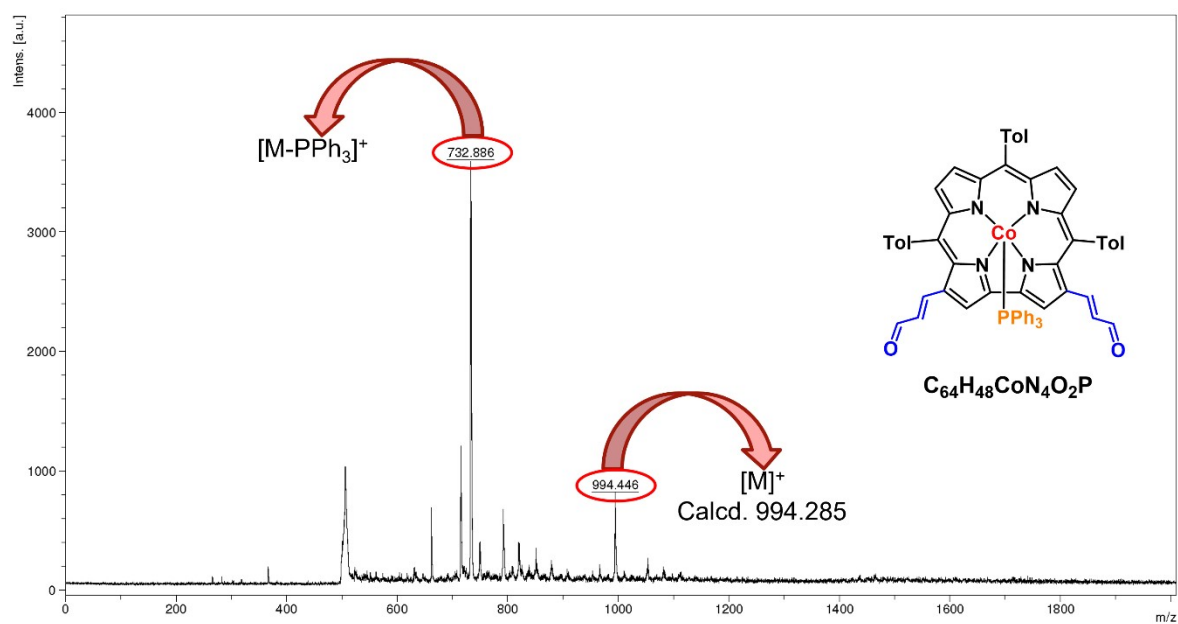
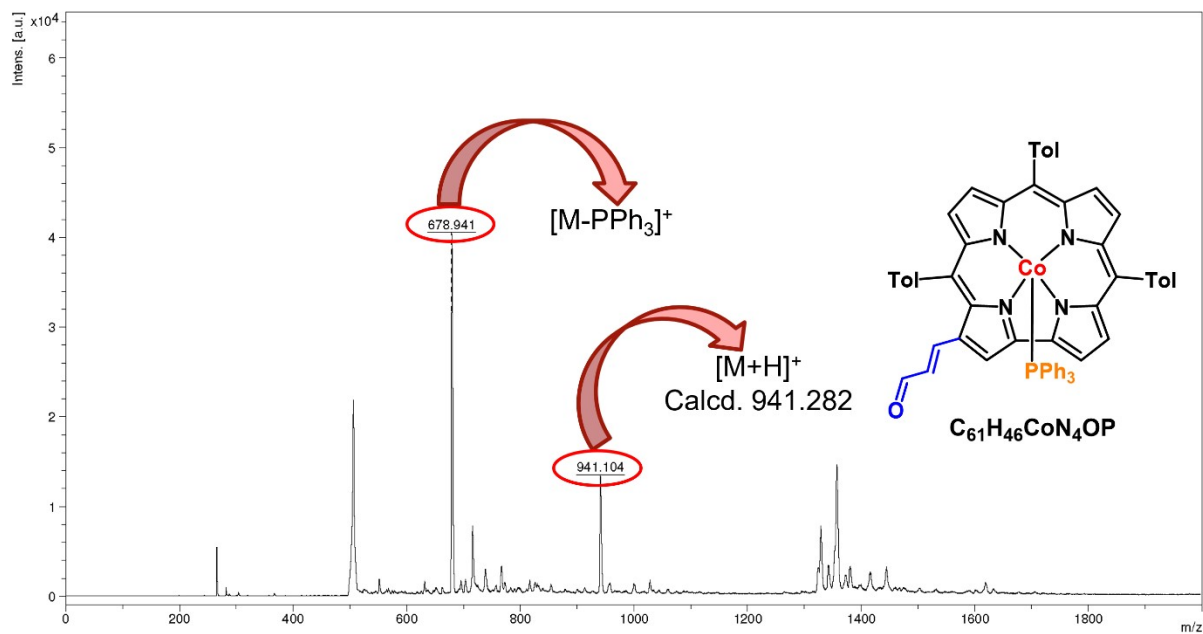
where  $(I_{\lambda}^{probe}/I_{\lambda}^{ref})_{Pump-On}$  is a ratio of corresponding pump and reference signals at a given wavelength, measured after the sample excitation. The term  $(I_{\lambda}^{probe}/I_{\lambda}^{ref})_{Pump-off}$  refers to the corresponding ratio to the unexcited sample.

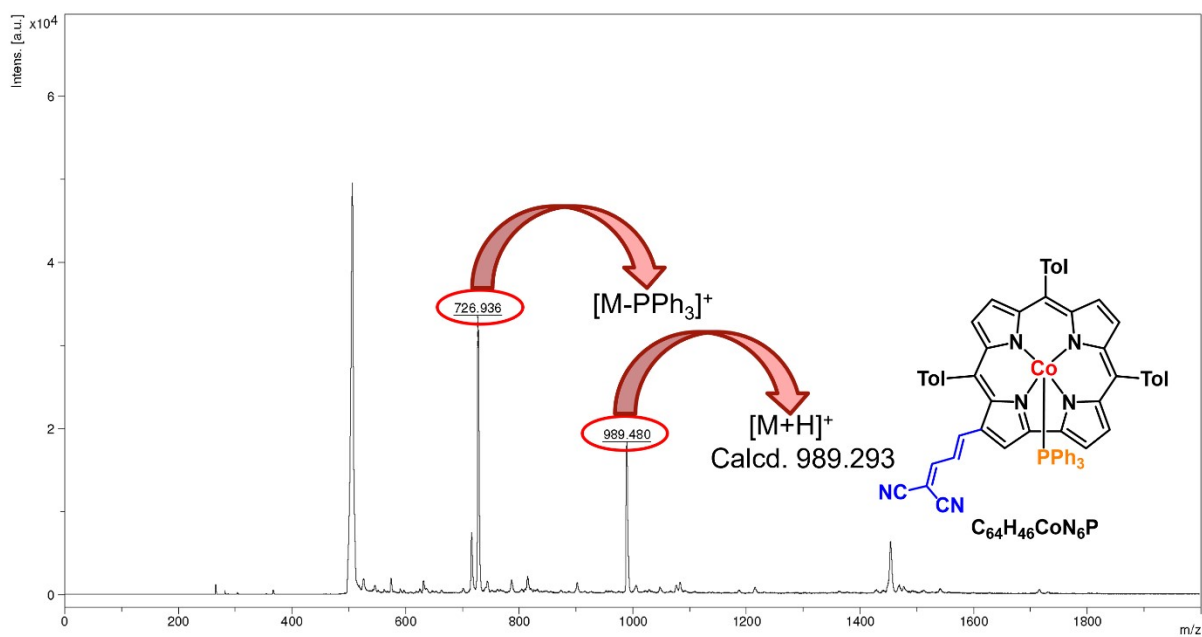
### Synthesis of mono- and disubstituted cobalt corroles

$\beta$ -Acrolein corroles **Co-1** and **Co-2** were prepared from the method described in the literature.<sup>1</sup>  $\beta$ -Dicyanobutadienyl corroles **Co-3** and **Co-4** were synthesized *via* Knoevenagel condensation of  $\beta$ -acrolein corroles and malononitrile in the presence of basic alumina using modified methods.<sup>2</sup> The purity of all the cobalt corroles was established through UV-visible (Fig. S1), proton NMR spectroscopy and mass spectrometry (Fig. S2–S5).

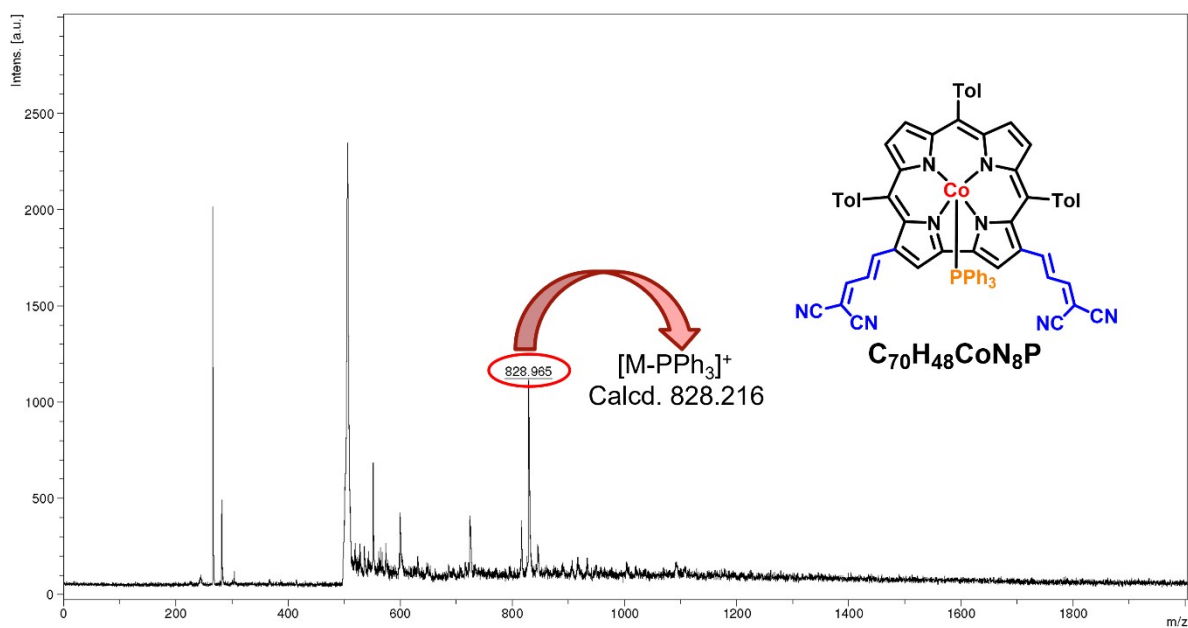


**Figure S1.** Comparative optical absorption spectra of **Co-1**, **Co-2**, **Co-3** and **Co-4** in DMF.

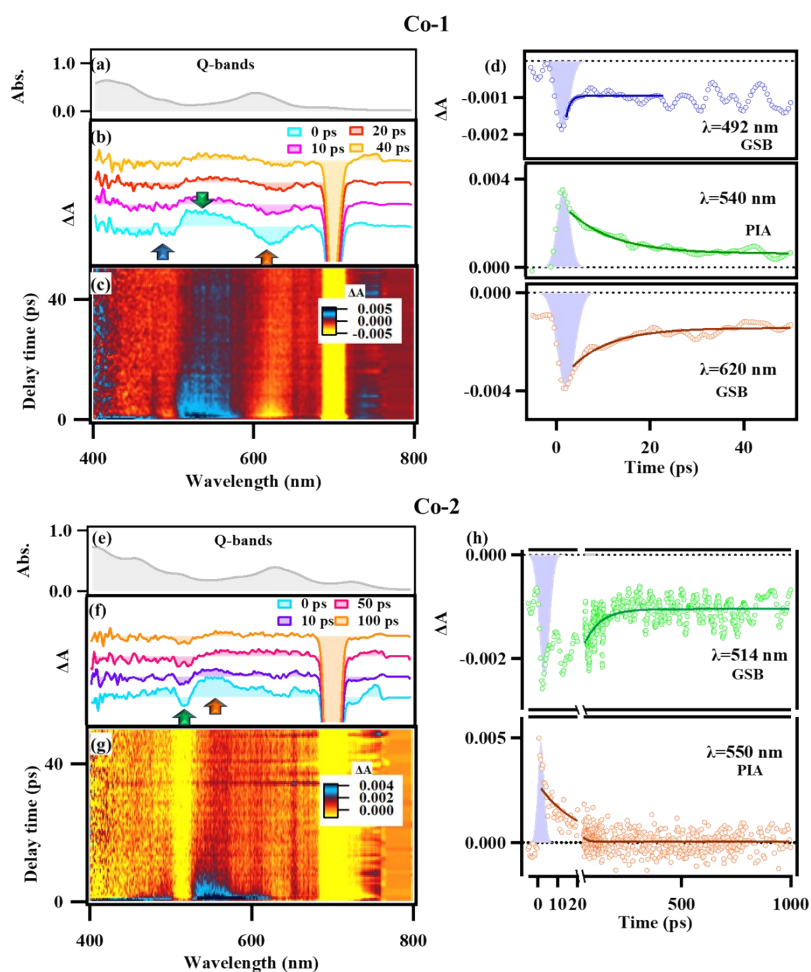




**Figure S4.** MALDI-TOF mass spectrum of Co-3 in CH<sub>2</sub>Cl<sub>2</sub> at 298 K.



**Figure S5.** MALDI-TOF mass spectrum of Co-4 in CH<sub>2</sub>Cl<sub>2</sub> at 298 K.



**Figure S6.** Transient absorption spectroscopy results of **Co-1** and **Co-2** corroles dissolved in DMF. (a, e) Linear absorbance spectrum of **Co-1** and **Co-2** indicating the Q-bands. (b, f) Transient difference absorbance ( $\Delta A$ ) spectrum of **Co-1** and **Co-2** at different delay time (arrows are the indicative of different probed regions). (c, g) Pump-probe delay time vs probe wavelength  $\Delta A$  mappings of **Co-1** and **Co-2**. (d, h)  $\Delta A$  temporal evolution of **Co-1** (monitored at 490, 540 and 620 nm) and **Co-2** (monitored at 514 and 550 nm) of various spectral regions. The pump beam: 350 nm (1 kHz, 120 fs) with pulse energy 0.2  $\mu\text{J}$ , and the probe beam: broadband white light continuum (1 kHz, 120 fs).

**Table S1** UV–vis spectral data of investigated cobalt corroles in DMF at 298 K.

Corrole	$\lambda_{\text{abs}}$ , nm
<b>Co-1</b>	374 (sh), 415 (6.34), 489 (sh), 603 (3.78), 692 (sh)
<b>Co-2</b>	405 (6.96), 452 (5.17), 509 (sh), 581 (sh), 630 (3.76), 725 (1.45)
<b>Co-3</b>	378 (6.83), 476 (5.95), 674 (7.87)
<b>Co-4</b>	357 (5.71), 452 (6.09), 535 (6.44), 642 (sh), 710 (9.43), 786 (sh), 854 (sh)

<sup>a</sup>Values in parentheses refer to  $\varepsilon \times 10^{-4} \text{ L mol}^{-1} \text{ cm}^{-1}$ , sh = shoulder.

**Table S2** Third-order nonlinear optical coefficients of investigated cobalt corroles extracted from Z-scan studies.

Corrole	$\beta$ ( $\times 10^{-13}$ ) ( $\text{m W}^{-1}$ )	$n_2$ ( $\times 10^{-19}$ ) ( $\text{m}^2 \text{ W}^{-1}$ )	Real [ $\chi^{(3)}$ ] ( $\times 10^{-13}$ ) (e.s.u.)	Im [ $\chi^{(3)}$ ] ( $\times 10^{-13}$ ) (e.s.u.)	Total [ $\chi^{(3)}$ ] ( $\times 10^{-13}$ ) (e.s.u.)
<b>Co-1</b>	0.67	1.67	1.28	0.03	1.28
<b>Co-2</b>	0.91	3.69	2.84	0.04	2.84
<b>Co-3</b>	6.19	1.96	1.51	0.31	1.54
<b>Co-4</b>	0.30	0.45	0.35	0.01	0.35

Laser parameters: 800 nm, 1 kHz, 120 fs and  $I_0 = 4.1 \times 10^{14} \text{ W m}^{-2}$ .



**Table S3** Comparison of NLO coefficients obtained for various some recently reported corrole derivatives employing fs and ps pulses excitation.

Corroles	Laser specifications	$\beta$ (cm W <sup>-1</sup> )	$\chi^{(3)}$ (esu)	Solvent	Ref.
Free base TPC and TTC corroles	680–800 nm, 1 kHz, 2 ps	$\sim 10^{-11}$	$\sim 10^{-12}$	CHCl <sub>3</sub>	3
<i>trans</i> -A <sub>2</sub> B Cobalt corroles	532 nm, 1 kHz, 4 ns	$\sim 10^{-9}$	$\sim 10^{-12}$	DMF	4
Free base (C <sub>6</sub> F <sub>5</sub> ) <sub>3</sub> and P-(OH) <sub>2</sub> (C <sub>6</sub> F <sub>5</sub> ) <sub>3</sub> corroles	600–800 nm, 1 kHz, 50 fs	–	$\sim 10^{-13}$	DMF	5
Free base <i>trans</i> -A <sub>2</sub> B corroles	800 nm, 80 MHz, 150 fs	$\sim 10^{-8}$	$\sim 10^{-9}$	CH <sub>2</sub> Cl <sub>2</sub>	6
Europium heteroleptic corrole–Pc triple-decker complexes	532 nm, 1 kHz, 20 ps	$\sim 10^{-5}$ esu	$\sim 10^{-10}$	toluene	7
Phosphorus(V) triazatetrabenzcorroles	800 nm, 80 MHz, 150 fs	–	–	CH <sub>2</sub> Cl <sub>2</sub>	8
Corrole-GO nanohybrids	532 nm, 1 kHz, 4 ns	$\sim 10^{-9}$	–	DMSO	9
Copper corroles	800 nm, 1 kHz, 120 fs	$\sim 10^{-11}$	$\sim 10^{-12}$	DMF	10
$\beta$ -Functionalized $\pi$ -extended cobalt corroles	800 nm, 1 kHz, 120 fs	$\sim 10^{-13}$	$\sim 10^{-12}$	DMF	<i>tw</i>

Ref. = reference, *tw* = this work.

**Table S4** Summary of transient absorption decay lifetimes (Laser details: pump: 350 nm (1 kHz, 120 fs) of pulse energy 0.2  $\mu$ J, and the probe is a broadband white light 400 nm to 800 nm (1 kHz, 120 fs)).

Corrole	$\lambda_{\text{probe}}$ (nm)	$\tau$ (ps)
<b>Co-1</b>	492 (GSB)	68
	540 (PIA)	10
	620 (GSB)	8
<b>Co-2</b>	514 (GSB)	96
	550 (PIA)	6
<b>Co-3</b>	510 (PIA)	4
	540 (GSB)	7
	580 (PIA)	9
	680 (GSB)	10
<b>Co-4</b>	520 (GSB)	31
	610 (GSB)	7

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